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ORGANIC REAGENTS FOR ORGANIC ANALYSIS

ORGANIC REAGENTS FOR METALS

AND FOR CERTAIN ACID RADICALS

4th Edition 1944

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BY THE STAFF OF THE
RESEARCH LABORATORY OF
HOPKIN & WILLIAMS LTD.

With a foreword by
DR. A. D. MITCHELL and DR. A. M. WARD

The volume consists of forty-four monographs on the use of organic reagents in inorganic analysis. Many of these substances, though worthy of adoption as routine reagents for the detection and determination of certain metals, have not yet found their way into the standard text books. This book places in the analyst's hands, in a concise form, much information which, on account of its recent nature, has hitherto appeared only in the technical journals. In addition, the techniques described have been subjected to careful examination in the research laboratories of the company to ensure their complete reliability.

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FOR
ORGANIC ANALYSIS

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PREFACE

WHILE investigating the preparation of a number of reagents for which a demand had arisen it became evident that the literature lacked an up-to-date review of their application to organic analysis. We venture to believe that such a review may serve a useful purpose in many laboratories concerned with organic chemical research and analysis and have been encouraged in this view by the continued demand for our previous publication "Organic Reagents for Metals". The two books have something in common in that they supplement existing text books with information on reagents from the more recent literature. In "Organic Reagents for Metals" the emphasis was rather on the reagent and its capabilities, a departure from the usual text book treatment. In the present volume we have followed the same principle, but have judged it an advantage in this case to introduce a preliminary section which constitutes a necessary guide in the rather more complicated circumstances.

The scope of the book embraces strictly what we have attempted to imply in a reasonably short title, the use of organic reagents in preparing derivatives of organic substances for purposes of identification by melting points. The preliminary stages of such an investigation and the alternative methods such as nitration, oxidation, reduction and bromination, applicable to many problems are not dealt with, but where a reagent has important quantitative uses of general application these are included.

The choice of reagents for inclusion has not always been easy, particularly where the literature provides a long series of reagents of closely similar type. Selection has been the outcome of practical re-investigation on the part of the compilers together with due consideration of the following factors :

(*a*) Accessibility of the reagent, which usually means, can it be produced at a reasonable price?

(*b*) Stability of the reagent.

(*c*) Simplicity, convenience and speed with which derivatives can be prepared and recrystallised in reasonably good yield.

(*d*) The derivatives should melt within a convenient temperature range, ideally between 100° and 250°.

(*e*) The melting points should differ sufficiently one from another for the derivatives of closely related compounds, e.g. in an homologous series or for *o*-, *m*- and *p*- isomers.

(*f*) The availability of an extensive series of melting points has been considered desirable but this has not been regarded as essential to the inclusion of some of the newer reagents since these, if they justify themselves, will eventually have further values determined.

(*g*) If the reagent provides derivatives having a free reactive group (e.g. carboxyl) which permits of titration this is considered a strong recommendation.

Possibly we have excluded some reagents which had a fair claim to a place, but all those that have come to our notice are reviewed briefly in Section I and literature references are included there for the guidance of readers whose interest extends beyond our own choice. The literature quoted in both sections includes only papers which feature the use of the reagents ; there are many others from which melting points have been taken.

Our practical work has given us opportunity to check some of the published melting points and to determine some new ones. We have found a disturbingly large number of cases where the literature and the reference books are contradictory or inaccurate on melting points. In many cases of contradiction we have satisfied ourselves as to the correct figure and we shall be grateful for any further amendments to the values quoted in our tables.

Certain reagents have been employed in the identification of sugars and of the amino derivatives of the fatty acids. Such methods, however, either depend upon characteristics other than melting points or are of an importance which is secondary to other accepted means of identification. For these reasons the substances in these two classes have received only passing mention and neither group appears in the tables.

It is assumed throughout that the analyst will prepare at least two derivatives of any unknown, and references are occasionally made in the text to this desirable practice.

Apart from the many periodicals quoted in the various bibliographies we are deeply indebted to the following books of reference.

Beilstein's Handbuch der organischen Chemie

Organic Analysis, Qualitative & Quantitative
E. DE BARRY BARNETT and P. C. L. THORNE

The Systematic Identification of Organic Compounds
R. L. SHRINER and R. C. FUSON

Reactions of Organic Compounds
W. J. HICKINBOTTOM

The Identification of Pure Organic Compounds
E. H. HUNTRESS and S. P. MULLIKEN

The present volume is the outcome of collaboration of the undersigned and his colleagues Dr. R. J. Shennan, M.Sc., F.R.I.C., and Mr. R. A. Reed, B.Sc., F.R.I.C.

W. C. JOHNSON,
Chief Chemist.

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NOTE

All the selected reagents are available from Hopkin & Williams, Ltd. A number of those described as " other reagents " will also be found in the catalogue of fine chemicals issued by the company. Enquiries for reagents which are not catalogued will receive careful consideration but it is evident that in very many cases the demand to be anticipated will not warrant manufacture.

GENERAL SURVEY

ACIDS, CARBOXYLIC

Selected Reagents

Aniline.
p-Bromophenacyl bromide.
p-Nitrobenzyl bromide.
Phenacyl bromide.
p-Toluidine.

Aniline and *p*-toluidine are the best reagents for the identification of the fatty acids, the final choice being governed by the particular acids to be differentiated. For the higher members of the fatty acid series there is no good reagent, and for the identification of these compounds it is necessary to resort to other methods. Generally speaking, the *p*-nitrobenzyl-, *p*-bromophenacyl-, and the phenacyl esters of the fatty acids are low melting point solids or liquids.

The *p*-bromophenacyl-, phenacyl- and *p*-nitrobenzyl esters of the polybasic and aromatic carboxylic acids are all easily prepared and well crystallised derivatives, and there is little to choose between the three compounds for identification purposes. The melting points of a large number of *p*-nitrobenzyl esters are available. *p*-Bromophenacyl esters are usually of higher melting points than the corresponding phenacyl esters.

Other Reagents

o-Toluidine.
p-Bromoaniline.
o-Bromo-*p*-toluidine.
2 : 4 : 6-Tribromoaniline.
β-Naphthylamine.
1-Bromo-2-naphthylamine.
P. W. Robertson, *J.C.S.*, **115**, 1210 (1919).

α-Naphthylamine.
P. W. Robertson, *J.C.S.*, **93**, 1033 (1908).

pp′-Diaminodiphenylmethane.
A. W. Ralston and M. R. McCorkle, *J.A.C.S.*, **61**, 1604 (1939).

o-Phenylenediamine.

R. Seka and R. H. Muller, *Monatsh.*, **57**, 97 (1931).
W. O. Pool, H. J. Harwood and A. W. Ralston, *J.A.C.S.*, **59**, 178 (1937).

Benzyl-*iso*-thiourea hydrochloride.

(for refs. *see* monograph, p. 42).

p-Chlorobenzyl-*iso*-thiourea hydrochloride.

B. T. Dewey and R. B. Sperry, *J.A.C.S.*, **61**, 3251 (1939).

p-Bromobenzyl-*iso*-thiourea hydrobromide.

B. T. Dewey and M. G. Shasky, *J.A.C.S.*, **63**, 3526 (1941).

p-Chlorophenacyl bromide.

W. L. Judefind and E. E. Reid. *J.A.C.S.*, **42**, 1043 (1920).

p-Iodophenacyl bromide.

W. L. Judefind and E. E. Reid. *J.A.C.S.*, **42**, 1043 (1920).
R. H. Hann, E. E. Reid and G. S. Jamieson. *J.A.C.S.*, **52**, 818 (1930).

p-Phenylphenacyl bromide.

N. L. Drake and J. Bronitsky. *J.A.C.S.*, **52**, 3715 (1930).

p-Nitrobenzyl chloride. }
p-Nitrobenzyl iodide. }

(*see p*-Nitrobenzyl bromide monograph, p. 69, for refs.).

The above reagents have all been employed for the characterisation of carboxylic acids but have not been considered worthy of inclusion. The first seven have been used in precisely the same way and for the same purposes as aniline and *p*-toluidine. As they offer no advantages over the last-named they appear superfluous.

o-Phenylenediamine forms easily prepared and nicely crystalline alkylbenziminazoles with the fatty acids, but unfortunately the melting points of the derivatives are too close to be of much service. *pp'*-Diaminodiphenylmethane condensates with the same class of acids suffer a similar failing.

Benzyl-*iso*-thiourea hydrochloride, *p*-chlorobenzyl-*iso*-thiourea hydrochloride and *p*-bromobenzyl-*iso*-thiourea hydrobromide have been proposed as carboxylic acid reagents ; the melting points of the derivatives are again too close to merit any special attention. The first-named has been extended to sulphonic acids with considerable advantage, and a monograph on this reagent for sulphonic acids is included.

Phenacyl bromide and its *p*-bromo derivative have been dealt with in detail. Other members of this class include *p*-chlorophenacyl-, *p*-iodophenacyl- and *p*-phenylphenacyl bromides which have been employed for the same purpose, and these have no outstanding merits. In fact far fewer derivatives have been prepared with these than with the two selected examples.

The only other carboxylic acid reagents are *p*-nitrobenzyl chloride and the corresponding iodide. These are employed in precisely the same way as the bromide and reference should be made to the monograph on *p*-nitrobenzyl bromide.

ALCOHOLS

Selected Reagents

Acetic anhydride.
3 : 5-Dinitrobenzoyl chloride.
α-Naphthyl *iso*-cyanate.
p-Nitrobenzoyl chloride.
p-Nitrophenyl *iso*-cyanate.
3-Nitrophthalic anhydride.
Phenyl *iso*-cyanate.
p-Xenyl *iso*-cyanate.

From our main standpoint of characterisation acetic anhydride may be disposed of immediately since the esters which it yields are generally liquid ; as a reagent for quantitative determination of hydroxyl it is, of course, of the utmost importance.

A point of practical significance affecting all the reagents in varying degree is that they require careful storage to protect them from atmospheric moisture. The liquid reagents phenyl *iso*-cyanate and more particularly α-naphthyl *iso*-cyanate possess some advantage on this score over the remainder, which are solids. 3 : 5-Dinitrobenzoyl chloride and *p*-nitrophenyl *iso*-cyanate very rapidly absorb moisture and become useless unless their containers are completely sealed after use.

The reagents vary also to a considerable extent with regard to the necessity for complete absence of moisture in the sample under examination, a condition not very readily achieved with the lower alcohols. Phenyl and *p*-nitrophenyl *iso*-cyanates in particular yield an excessive proportion of substituted ureas if moisture is present in the reaction mixture. On the other hand, *p*-nitrobenzoyl chloride may be used for dilute solutions of alcohols, while the remaining members of the above list are not too adversely affected by traces of water.

For relative convenience of preparation of derivatives phenyl and α-naphthyl *iso*-cyanates possess considerable advantages ; the reactions take place very readily under simple conditions and the products crystallise well from the recommended solvents.

The melting points of most derivatives of the monohydric alcohols are rather low, though this is not accompanied by any general difficulty in crystallisation as is liable to be the case with other classes of compound. Higher melting points are obtained with α-naphthyl *iso*-cyanate and with *p*-xenyl *iso*-cyanate, and the lower melting esters obtained with 3 : 5-dinitrobenzoyl chloride may be combined with α-naphthylamine to yield addition compounds of higher melting point. The esters obtained with 3-nitrophthalic anhydride are also of higher melting point than the average, but this reagent has an important additional advantage in that the derivatives have one free carboxyl group which may be titrated, thus affording a means of determining the molecular weight of the alcohol.

The differentiation obtainable on melting points is generally fairly good amongst the lower alcohols and there are no reagents of outstanding merit from this point of view. A study of the tables is the best guide to individual cases. For alcohols containing more than seven carbon atoms the melting point differences are uniformly poor and the series for each reagent is lacking in completeness.

Other Reagents

o-Nitrophenyl *iso*-cyanate.
m-Nitrophenyl *iso*-cyanate.
3 : 5-Dinitrophenyl *iso*-cyanate.
F. Hoeke. *Rec. trav. chim.*, **54**, 505 (1935).

p-Methoxyphenyl *iso*-cyanate.
3 : 4-Dimethoxyphenyl *iso*-cyanate.
O. Brunner and R. Wöhrl. *Monatsh.*, **63**, 377 (1933).

4-Iododiphenyl-4′-*iso*-cyanate.
S. Kawai and K. Tamura. *Inst. Phys. and Chem. Res., Tokyo*, **13**, No. 252 (1930).

2 : 4 : 6-Trinitrobenzoyl chloride.
M. C. Chang and C. H. Kao. *J. Chinese Chem. Soc.*, **3**, 251 (1935).

Anthraquinone-2-carboxylic acid chloride.
T. Reichstein. *Helv. Chim. Acta*, **9**, 803 (1926).

1-Nitroanthraquinone-2-carboxylic acid chloride.
P. P. T. Sah and T. S. Ma. *J. Chinese Chem. Soc.*, **1**, 51 (1933).

Bromomethylphthalimide.
H. H. Hopkins. *J.A.C.S.*, **45**, 541 (1923).

Phthalic anhydride.

The *iso*-cyanates are already represented by those which appear to offer the greatest advantages.

There is no reason to prefer 2 : 4 : 6-trinitrobenzoyl chloride to the more readily accessible 3 : 5-dinitrobenzoyl chloride.

The two anthraquinone compounds appear to have useful characteristics but no satisfactory methods are available for their commercial production.

Bromomethylphthalimide requires anhydrous alcohols when preparing derivatives.

Phthalic anhydride yields esters with melting points too low for convenient manipulation ; its 3-nitro derivative is far more satisfactory.

ALDEHYDES AND KETONES

Selected Reagents

Benzaldehyde (ketomethylenes only).
Dimedone (aldehydes only).
2 : 4-Dinitrophenylhydrazine.
Hydroxylamine hydrochloride.
p-Nitrophenylhydrazine.
Phenylhydrazine hydrochloride.
4-Phenylsemicarbazide.
Semicarbazide hydrochloride.
p-Thiocyanophenylhydrazine hydrochloride.
Thiosemicarbazide.

The older reagents, hydroxylamine, phenylhydrazine and semicarbazide hydrochlorides have one advantage in common : that a fairly comprehensive range of melting points is available in each case and for this reason, if for no other, one or other of these reagents would be employed in the first instance. The first two have considerable limitations in that, for example, the carbonyl compounds of low molecular weight give derivatives which are liquid or of very low melting point, while phenylhydrazones decompose rather rapidly. *p*-Nitro- and 2 : 4-dinitro-phenylhydrazine yield higher melting derivatives even with the lower members of the series; both these reagents have a comprehensive series of melting points and may claim equal importance with those mentioned above.

For **quantitative** purposes hydroxylamine hydrochloride retains its importance as the basis of the standard volumetric procedure. Other quantitative methods have been devised in which phenylhydrazine, *p*-nitrophenylhydrazine and 2 : 4-dinitrophenylhydrazine are used. Thiosemicarbazones form metallic compounds and are thus adaptable to the determination of molecular weights. Formaldehyde may very conveniently be determined with dimedone, which is also a very sensitive and selective reagent for this aldehyde.

Dimedone has the distinction of providing two derivatives from each aldehyde and, since it does not react with ketones, may be found of special use where mixtures are concerned.

Other Reagents

o-Bromobenzhydrazide.
P. P. T. SAH *et al.* *Sci. Rep. Nat. Tsing Hua Univ.*, **3**, 555 (1936).

m-Bromobenzhydrazide.
P. P. T. SAH *et al.* *J. Chinese Chem. Soc.*, **4**, 70 (1936).

p-Bromobenzhydrazide.
P. P. T. SAH *et al.* *Sci. Rep. Nat. Tsing Hua Univ.*, **3**, 280 (1935).

o-Chlorobenzhydrazide.
T. H. SUN and P. P. T. SAH. *Sci. Rep. Nat. Tsing Hua Univ.*, **2**, 360 (1934).

m-Chlorobenzhydrazide.
P. P. T. SAH and C. S. WU. *Sci. Rep. Nat. Tsing Hua Univ.*, **3**, 445 (1936).

p-Chlorobenzhydrazide.
G. SHIH and P. P. T. SAH. *Sci. Rep. Nat. Tsing Hua Univ.*, **2**, 353 (1934).

3 : 5-Dinitrobenzhydrazide.
P. P. T. SAH and T. S. MA. *J. Chinese Chem. Soc.*, **11**, 40 (1934).

l-Menthydrazide.
R. B. Woodward, T. P. Kohman and G. C. Harris. *J.A.C.S.*, **63**, 120 (1941).

β-Naphthydrazide.
P. P. T. Sah. *J. Chinese Chem. Soc.*, **4**, 63 (1936).

o-, *m*- and *p*-Nitrobenzene sulphonhydrazide.
A. A. M. Witte. *Rec. trav. chim.*, **51**, 302 (1932).

o-Nitrobenzhydrazide.
P. P. T. Sah and C. H. Kao. *Sci. Rep. Nat. Tsing Hua Univ.*, **3**, 461 (1936).
P. P. T. Sah and W. H. Yin. *Rec. trav. chim.*, **59**, 241 (1940).

m-Nitrobenzhydrazide.
H. H. Strain. *J.A.C.S.*, **57**, 758 (1935).
P. P. T. Sah and C. H. Kao. *Sci. Rep. Nat. Tsing Hua Univ.*, **3**, 461 (1936).

p-Nitrobenzhydrazide.
P. Chen. *J. Chinese Chem. Soc.*, **3**, 251 (1935).

Girard's Reagent P (Pyridinium acetohydrazide chloride).

Girard's Reagent T (Trimethylammonium acetohydrazide chloride).
A. Girard and G. Sandulesco. *Helv. Chim. Acta*, **19**, 1095 (1936).

1-Benzyl-1-phenylhydrazine.
Van Ekenstein and Lobry de Bruyn. *Rec. trav. chim.*, **15**, 225 (1896) ; A. Hofmann. *Ann.*, **366**, 277 (1909).

p-Bromophenylhydrazine hydrochloride.
H. Biltz and F. Sieden. *Ann.*, **324**, 315 (1902).

Carboxy-methyl-hydrazine.
M. Anchel and R. Schoenheimer. *J. Biol. Chem.*, **114**, 544 (1936).

o-Carboxy-phenylhydrazine.
S. Veibel *et al.* *B.C.A.*, A II, 33 (1944).

m-Carboxy-phenylhydrazine.
R. Willstätter *et al.* *Ann.*, **418**, 127 (1919).

p-Carboxy-phenylhydrazine.
M. Anchel and R. Schoenheimer. *J. Biol. Chem.*, **114**, 539 (1936).
S. Veibel *et al.* *B.C.A.*, A II, 33 (1944).

p-Chlorophenylhydrazine hydrochloride.
P. P. T. Sah *et al.* *Sci. Rep. Nat. Tsing Hua Univ.*, **2**, 8 (1933).

asym-Diphenylhydrazine hydrochloride.
E. Fischer. *Ann.*, **190**, 175 (1878).
A. D. Maurenbrecher. *Ber.*, **39**, 3584 (1906).

1-Methyl-1-phenylhydrazine.
H. R. Stevens and F. W. Ward. *J.C.S.*, **125**, 1328 (1924).
C. Neuberg, *Ber.*, **35** 959, 2626 (1902).

α-Naphthylhydrazine hydrochloride.
E. Fischer. *Ann.*, **232**, 237 (1886).

β-Naphthylhydrazine hydrochloride.
E. Fischer. *Ann.*, **232**, 242 (1886).

Nitroguanylhydrazine.
W. F. Whitmore *et al.* *J.A.C.S.*, **57**, 706 (1935).

o-Nitrophenylhydrazine.
A. Bischler. *Ber.*, **22**, 2801 (1889).
A. van Ekenstein and J. J. Blanksma. *Rec. trav. chim.*, **24**, 37 (1905).

m-Nitrophenylhydrazine.
A. Bischler and S. Brodsky. *Ber.*, **22**, 2809 (1889).
A. van Ekenstein and J. J. Blanksma. *Rec. trav. chim.*, **24**, 36 (1905).

Phenylhydrazine-*p*-sulphonic acid.
H. Biltz, A. Maué and F. Sieden. *Ber.*, **35**, 2004 (1902).

o-Tolylhydrazine hydrochloride.
P. P. T. Sah and T. S. Ma. *Sci. Rep. Nat. Tsing Hua Univ.*, **1**, 261 (1932).

m-Tolylhydrazine hydrochloride.
P. P. T. Sah and C. Z. Tseu. *Sci. Rep. Nat. Tsing Hua Univ.*, **3**, 403, 409 (1936).

p-Tolylhydrazine hydrochloride.
P. P. T. Sah and H. H. Lei. *Sci. Rep. Nat. Tsing Hua Univ.*, **2**, 1 (1933).

2 : 4 : 6-Trinitrophenylhydrazine.
A. Purgotti. *Gazz.*, **24** [1], 113 (1894).

p-Xenylhydrazine.
H. Müller. *Ber.*, **27**, 3106 (1894).

Benzylsemicarbazide.
I. V. Hopper. *J. Roy. Tech. Coll.* (*Glasgow*), **2** (1), 52 (1929).

2 : 4-Dinitrophenylsemicarbazide.
R. Barré and L. Piché. *Canad. J. Res.*, **19B**, 158 (1941); **20B**, 17 (1942).

3 : 5-Dinitrophenylsemicarbazide.
P. P. T. Sah and P. C. Tao. *J. Chinese Chem. Soc.*, **4**, 506 (1936).

α-Naphthylsemicarbazide.
P. P. T. Sah and S. H. Chiang. *J. Chinese Chem. Soc.*, **4**, 496 (1936).

β-Naphthylsemicarbazide.
P. P. T. Sah and P. C. Tao. *J. Chinese Chem. Soc.*, **4**, 501 (1936).

p-Nitrobenzylsemicarbazide,
p-Nitrophenylsemicarbazide,
p-Nitroxenylsemicarbazide.
R. Barré and L. Piché. *Canad. J. Res.*, **19B**, 158 (1941); **20B**, 17 (1942).

o-Tolylsemicarbazide.
H. H. Lei, P. P. T. Sah and C. Shih. *J. Chinese Chem. Soc.*, **3**, 246 (1935).

m-Tolylsemicarbazide.
P. P. T. Sah *et al.* *J. Chinese Chem. Soc.*, **4**, 187 (1936).

p-Tolylsemicarbazide.

P. P. T. Sah and H. H. Lei. *J. Chinese Chem. Soc.*, **2**, 167 (1934).

p-Xenylsemicarbazide.

P. P. T. Sah and I. S. Kao. *Rec. trav. chim.*, **58**, 459 (1939).

Phenylsemioxamazide.

P. P. T. Sah and W. P. Han. *Sci. Rep. Nat. Tsing Hua Univ.*, **3**, 468 (1936).

Semioxamazide.

L. G. Radcliffe. *Perfumery and Essential Oil Rec.*, **10**, 39 (1919).

Aminoguanidine.

R. Baeyer. *Ber.*, **27**, 1919 (1894).

O-Aminoglycollic acid.

E. Borek and H. T. Clarke. *J.A.C.S.*, **58**, 2020 (1936).
M. Anchel and R. Schoenheimer. *J. Biol. Chem.*, **114**, 542 (1936).

The hydrazides are not represented in the selected reagents since, as a class, they yield derivatives with carbonyl compounds which do not crystallise satisfactorily. Girard's reagents are employed for isolation and not for purposes of identification.

The extensive series of substituted phenylhydrazines is represented by three very useful members. Most of the others seem to have evoked little interest since their publication, while certain of them suffer positive disadvantages. For example, *asym*-diphenylhydrazine hydrochloride and *o*-nitrophenylhydrazine are unstable, while the tolylhydrazines, particularly the ortho compound, yield unstable derivatives. Phenylhydrazine-*p*-sulphonic acid gives derivatives which melt unduly high with decomposition. 2 : 4 : 6-Trinitrophenylhydrazine was investigated by an author whose melting points have been found quite unreliable.

The substituted semicarbazides have received considerable attention but offer no significant advantage over semicarbazide itself except perhaps with certain of the normal aliphatic aldehydes up to C_{10}. Melting points for the derivatives of a number of semicarbazides are tabulated in the paper cited under *p*-xenylsemicarbazide.

The derivatives of semioxamazide were found to be not readily prepared or purified and their melting points inconveniently high. Aminoguanidine appears to have become obsolete as a reagent. No method is available for the preparation of *O*-aminoglycollic acid on a satisfactory scale.

ALKALOIDS

Selected Reagents

Picric acid.
Styphnic acid.

Few reagents are available which yield derivatives having definite melting points, the best undoubtedly being picric and styphnic acids. The picrates and styphnates are easily prepared and, with the exception of those from some of the cinchona alkaloids, crystallise well. It is worthy of note that large discrepancies occur in the literature over the melting points of some derivatives ; thus, papaverine picrate is quoted by two different authors as having melting points, 183° and 154°.

The crystalline forms of these derivatives have been stated by some workers to be better criteria than the melting points.

Other Reagent

Picrolonic acid.

H. Matthes *et al.* *Arch. Pharm.*, **245**, 112 (1907).
L. Kofler and F. A. Müller, *Mikrochem.*, **22**, 43 (1937).

The picrolonates of the alkaloids are unsatisfactory derivatives since their melting points lie very close together and melting is accompanied by decomposition.

AMIDES

Selected Reagent

Xanthydrol.

This reagent is very useful for identifying **aliphatic** amides when hydrolysis yields no useful product.

Although **aromatic** amides yield solid acids on hydrolysis, the reagent still has a very useful confirmatory function.

Other Reagent

Phthalyl chloride.

T. W. Evans and W. M. Dehn, *J.A.C.S.*, **51**, 3651 (1929).

This reagent is of little *general* use since only four derivatives are described in the above paper.

AMINES, PRIMARY

Selected Reagents

Acetic anhydride.
Benzaldehyde.
Benzenesulphonyl chloride.
Benzoyl chloride.
2 : 4-Dinitrochlorobenzene.
Formic acid.
α-Naphthyl *iso*-cyanate.
α-Naphthyl *iso*-thiocyanate.
p-Nitrobenzaldehyde.
p-Nitrophenyl *iso*-cyanate.
Phenyl *iso*-thiocyanate.
Phthalic anhydride.
Picric acid.
Picryl chloride.
p-Toluenesulphonyl chloride.
1 : 3 : 5-Trinitrobenzene.
2 : 4 : 5-Trinitrotoluene.

The number of reagents for primary amines which have been investigated is greater than for any other class of compound. In the above list of seventeen selected reagents we have included only those which appear to possess particular merit.

Most reagents for **aliphatic** primary amines yield derivatives of rather low melting point, and although benzoyl chloride may find occasional application, acetic anhydride is almost useless in this series. More generally useful reagents are 2 : 4-dinitrochlorobenzene, *p*-toluenesulphonyl chloride and phenyl *iso*-thiocyanate, while phthalic anhydride, though giving some very low melting points, is of exceptional merit for the disparity throughout the range. The following yield derivatives of higher melting points: picric acid, α-naphthyl *iso*-thiocyanate and 2 : 4 : 5-trinitrotoluene.

Since some of the lower aliphatic amines are commonly encountered in aqueous solution, picric acid should be mentioned as a reagent capable of direct application under these conditions.

When it is a question of characterising an **aromatic** amine the first choice of reagent would almost invariably be either acetic anhydride or benzoyl chloride, since there are far more melting points available for acetyl and benzoyl compounds than for the derivatives yielded by any of the other reagents. These two reagents are also of simple application and afford well-crystallised derivatives though the benzoyl compounds are occasionally difficult to solidify owing to occlusion of sodium benzoate. Formic acid and phthalic anhydride should also be considered as useful alternatives to acetic anhydride, for in both these cases a good range of melting points is available.

The aromatic *o*-nitroamines require a catalyst to induce condensation with acetic anhydride, but formic acid yields derivatives readily without the necessity of a catalyst. 2 : 4-Dinitrochlorobenzene and picryl chloride are not recommended for the nitroamines since few melting points are available.

As a secondary choice for aromatic primary amines the following are of equal merit on general considerations, while points of individual advantage will arise from a study of the monographs and melting point tables.

2 : 4-Dinitrochlorobenzene.
p-Nitrobenzaldehyde.
Phenyl *iso*-thiocyanate.
Picric acid.
Picryl chloride.
p-Toluenesulphonyl chloride.

Picryl chloride has a distinctive advantage in that it frequently gives differently coloured derivatives with isomeric compounds. Thus *o*- and *p*-anisidines can be distinguished by the colour alone of their picramides. For the toluidines 2 : 4-dinitrochlorobenzene and *p*-nitrobenzaldehyde may be recommended.

Benzidine and *o*-tolidine can readily be differentiated by means of benzaldehyde but with many other amines this reagent gives oily derivatives.

Primary, secondary and tertiary amines may be separated by the use of benzene- or *p*-toluene-sulphonyl chloride and this is the only reason for the inclusion of the former reagent.

Other Reagents

Benzylsulphonyl chloride.

E. Fromm and J. de S. Palma. *Ber.*, **39**, 3308 (1906).
T. B. Johnson and J. A. Ambler. *J.A.C.S.*, **36**, 372 (1914).
C. S. Marvel and H. B. Gillespie. *J.A.C.S.*, **48**, 2943 (1926).

p-Bromobenzenesulphonyl chloride.

W. Ssolonina. *J. Russ. Phys. Chem. Soc.*, **31**, 643 (1899); *C.Z.*, ii, 867 (1899).
C. S. Marvel and F. E. Smith. *J.A.C.S.*, **45**, 2696 (1923).

Methanesulphonyl chloride.

C. S. Marvel, M. D. Helfrick and J. P. Belsley. *J.A.C.S.*, **51**, 1272 (1929).

m-Nitrobenzenesulphonyl chloride.

W. Ssolonina. *J. Russ. Phys. Chem. Soc.*, **31**, 640 (1899); *C.Z.*, ii, 867 (1899).
F. D. Chattaway. *J.C.S.*, **85**, 1181 (1904).
O. N. Witt and H. Truttwin. *Ber.*, **47**, 2786 (1914).
C. S. Marvel, F. L. Kingsbury and F. E. Smith. *J.A.C.S.*, **47**, 166 (1925).

m-Bromobenzazide.

P. P. T. Sah and L. H. Chang. *Rec. trav. chim.*, **58**, 8 (1939).

p-Bromobenzazide.

P. P. T. Sah, C. H. Kao and S. M. Wang. *J. Chinese Chem. Soc.*, **4**, 193 (1936).

m-Chlorobenzazide.

P. P. T. Sah. *J. Chinese Chem. Soc.* **4**, 514 (1936).

3 : 5-Dinitrobenzazide.

P. P. T. Sah and T. S. Ma. *J. Chinese Chem. Soc.*, **2**, 159 (1934).

3 : 5-Dinitro-4-methyl benzazide.

P. P. T. Sah. *Rec. trav. chim.*, **59**, 1008 (1939).

β-Naphthazide.

P. P. T. Sah. *J. Chinese Chem. Soc.*, **5**, 103 (1937).

m-Nitrobenzazide.

K. Meng and P. P. T. Sah. *J. Chinese Chem. Soc.*, **4**, 75 (1936).

p-Nitrobenzazide.

P. P. T. Sah. *Rec. trav. chim.*, **59**, 231 (1940).

p-Bromophenyl *iso*-thiocyanate.

P. P. T. Sah, S. H. Chiang and H. H. Lei. *J. Chinese Chem. Soc.*, **2**, 225 (1934).

p-Chlorophenyl *iso*-thiocyanate,
β-Naphthyl *iso*-thiocyanate.

E. L. Brown and N. Campbell. *J.C.S.*, 1699 (1937).

m-Nitrobenzoyl *iso*-thiocyanate.

W. L. Tung *et al.* *Sci. Rep. Nat. Tsing Hua Univ.*, **A3**, 285 (1935).

m-Nitrophenyl *iso*-thiocyanate.

P. P. T. Sah and H. H. Lei. *J. Chinese Chem. Soc.*, **2**, 153 (1934).
E. L. Brown and N. Campbell. *J.C.S.*, 1699 (1937).

o-Tolyl *iso*-thiocyanate.

T. OTTEBACHER and F. C. WHITMORE. *J.A.C.S.*, **51**, 1909 (1929).
M. F. GOEHRING and M. E. POTTEBAUM. *Amer. J. Pharm.*, **106**, 344 (1934).

p-Xenyl *iso*-thiocyanate.

E. L. BROWN and N. CAMPBELL. *J.C.S.*, 1699 (1937).

3 : 5-Dinitrophenyl *iso*-cyanate,
o-Nitrophenyl *iso*-cyanate,
m-Nitrophenyl *iso*-cyanate.

F. HOEKE. *Rec. trav. chim.*, **54**, 505 (1935).

p-Xenyl *iso*-cyanate.

M. J. VAN GELDEREN. *Rec. trav. chim.*, **52**, 976 (1933).

2 : 4-Dinitrobenzoic acid.

C. A. BUEHLER and J. D. CALFEE. *Ind. Eng. Chem.* (*Anal.*), **6**, 351 (1934).

3 : 5-Dinitrobenzoic acid.

C. A. BUEHLER, E. J. CURRIER and R. LAWRENCE. *Ind. Eng. Chem.* (*Anal.*), **5**, 277 (1933).

3 : 5-Dinitro-*o*-toluic acid.

P. P. T. SAH and C. H. TIEN. *J. Chinese Chem. Soc.*, **4**, 490 (1936).

3 : 5-Dinitro-*p*-toluic acid.

P. P. T. SAH and K. YUIN. *J. Chinese Chem. Soc.*, **5**, 129 (1937).

Ethyl sulphone diacetate.

J. P. ALDEN and B. HOUSTON. *J.A.C.S.*, **56**, 413 (1934).

Nitrourea.

P. P. T. SAH. *Sci. Rep. Nat. Tsing Hua Univ.*, **2**, 227 (1934).

2 : 4 : 6-Trinitrotoluene.

P. PFEIFFER. "*Organische Molekülverbindungen*", pp. 226, 239 (1922).

Benzyl-, *p*-bromobenzene-, methane- and *m*-nitrobenzene-sulphonyl chlorides all give derivatives of the type given by benzene- and *p*-toluene-sulphonyl chlorides and offer no general advantage over the latter reagents.

Many substituted benzazides have been proposed by P. P. T. Sah and his co-workers as reagents for primary amines. The reagents, however, are not particularly stable and do not possess sufficient redeeming features to obviate this defect.

The *iso*-cyanates given above are of a class already represented by α-naphthyl and *p*-nitrophenyl *iso*-cyanates. The use of *o*-nitrophenyl *iso*-cyanate is not recommended but the others may find use in special circumstances. Similarly the *iso*-thiocyanates have been represented by those two which appeared most useful.

Another class of proposed reagents comprises 3 : 5-dinitro-*o*-

toluic acid, 3 : 5-dinitro-*p*-toluic acid, 2 : 4-dinitro-benzoic acid and 3 : 5-dinitrobenzoic acid. All form salts with primary amines and as reagents they may find useful application in special cases but for general use more noteworthy reagents are already available.

Ethyl sulphone diacetate, $SO_2(CH_2COOC_2H_5)_2$, has been employed for the identification of ten aliphatic primary amines but the melting points of the derivatives, $SO_2(CH_2CONHR)_2$, are not sufficiently characteristic. From this viewpoint phthalic anhydride and picric acid are to be preferred as reagents.

Nitrourea does not merit selection since the alkyl ureas that are formed from aliphatic amines are deliquescent and difficult to purify by crystallisation.

2 : 4 : 6-Trinitrotoluene forms addition compounds with many amines but has no advantage over 1 : 3 : 5-trinitrobenzene and indeed has received less attention.

AMINES, SECONDARY

Selected Reagents

Acetic anhydride.
Benzenesulphonyl chloride.
Benzoyl chloride.
2 : 4-Dinitrochlorobenzene.
Formic acid.
α-Naphthyl *iso*-cyanate.
α-Naphthyl *iso*-thiocyanate.
p-Nitrophenyl *iso*-cyanate.
Picric acid.
Picryl chloride.
p-Toluenesulphonyl chloride.
1 : 3 : 5-Trinitrobenzene.

Aliphatic secondary amines are best characterised by α-naphthyl and *p*-nitrophenyl *iso*-cyanates, α-naphthyl *iso*-thiocyanate, picric acid and picryl chloride. The other reagents yield either oily products or low melting solids.

For general use in the identification of aromatic secondary amines, benzoyl chloride, picric acid and picryl chloride are to be preferred. For special cases, attention should be paid to the melting point table, p. 129 ; thus diphenylamine is most readily characterised as the formyl derivative.

Separation of the secondary amines in a pure condition can readily be achieved by the use of benzene- or *p*-toluene-sulphonyl chloride, and in some cases the derivatives themselves are of use.

Acetic anhydride and 1 : 3 : 5-trinitrobenzene are included for the number of derivatives described.

Other Reagents

Benzylsulphonyl chloride.

J. B. Johnson and J. A. Ambler. *J.A.C.S.*, **36**, 372 (1914).
C. S. Marvel and H. B. Gillespie. *J.A.C.S.*, **48**, 2943 (1926).

p-Bromobenzenesulphonyl chloride.

W. Ssolonina. *J. Russ. Phys. Chem. Soc.*, **31**, 643 (1899) ; *C.Z.*, ii, 867 (1899).
C. S. Marvel and F. E. Smith. *J.A.C.S.*, **45**, 2696 (1923).

m-Nitrobenzenesulphonyl chloride.

W. Ssolonina. *J. Russ. Phys. Chem. Soc.*, **31**, 640 (1899) ; *C.Z.*, ii, 867 (1899).
C. S. Marvel, F. L. Kingsbury and F. E. Smith. *J.A.C.S.*, **47**, 166 (1925).

p-Nitrobenzyl bromide.

E. Lyons. *J. Amer. Pharm. Assoc.*, **21**, 224 (1932).

The sulphonyl chlorides given above have all been used in precisely the same way as those given as selected reagents (benzene- and *p*-toluene-sulphonyl chlorides) and possess no advantage over the latter.

p-Nitrobenzyl bromide has been used only to characterise ethylaniline and diphenylamine.

AMINES, TERTIARY

Selected Reagents

Methyl iodide.
Picric acid.
Styphnic acid.
1 : 3 : 5-Trinitrobenzene.

The first choice of a reagent for tertiary amines is undoubtedly picric acid. A wide range of melting points of picrates is available and the derivatives are readily and easily prepared, titration giving a further characteristic. Moreover, an aqueous solution of the amine is no deterrent to the use of this reagent, as it is with methyl iodide and trinitrobenzene.

If the anhydrous amine is encountered or may easily be obtained, methyl iodide may also be employed to good effect, since many such derivatives have been described.

Styphnic acid has a useful function in isolated cases.

1 : 3 : 5-Trinitrobenzene has no special virtue in this connection.

Other Reagent

Methyl *p*-toluene sulphonate.

C. S. Marvel, E. W. Scott and K. L. Amstutz. *J.A.C.S.*, **51**, 3638 (1929).

This reagent has been tested and found wanting. In spite of the claims of its proposers, most of our final products were oily, and when a crystalline solid was obtained, a repeat experiment gave a solid having an entirely different melting point. Purification of the reagent and drying the benzene immediately before use as solvent effected no improvement. As an added disadvantage, all solid derivatives obtained were highly deliquescent.

Halides such as ethyl iodide and benzyl chloride have been used to identify tertiary amines but are omitted here owing to the small number of derivatives reported.

BARBITURIC ACIDS

Selected Reagents

p-Nitrobenzyl bromide.
Xanthydrol.

Two reagents only have been employed for the identification of barbituric acids. For *N*-substituted barbituric acids *p*-nitrobenzyl bromide must be used; for barbituric acids with mono- or di- substitution in the 5-position, these reagents are of equal merit.

ETHERS

Selected Reagents

3 : 5-Dinitrobenzoyl chloride.
Picric acid.
1 : 3 : 5-Trinitrobenzene.

Aromatic or aromatic-aliphatic ethers are best characterised by the preparation of the picrate. 1 : 3 : 5-Trinitrobenzene may be used in a few cases to confirm the ether's identity.

Symmetrical aliphatic ethers may be characterised by fission with zinc chloride and subsequent preparation of the 3 : 5-dinitrobenzoate of the alcohol produced.

Other Reagent

Chlorosulphonic acid.
E. H. Huntress and F. H. Carten. *J.A.C.S.*, **62**, 603 (1940).

Aromatic ethers may also be identified by treatment with chlorosulphonic acid to form the sulphonyl chloride, which is then treated with ammonia or ammonium carbonate to form the easily purified sulphonamide, having a definite melting point. The extremely corrosive nature of this reagent constitutes a disadvantage which outweighs its otherwise useful functions.

HALIDES

Selected Reagents

α-Naphthyl *iso*-cyanate.
Phenyl *iso*-cyanate.

Of the two reagents the α-naphthyl compound is somewhat more convenient to use: the naphthalides crystallise rather more satisfactorily and have higher melting points. It is recommended, therefore, that this reagent be employed whenever the melting point table includes the substance believed to be in question. Phenyl *iso*-cyanate is a very satisfactory alternative and has the advantage that a considerably greater number of anilides have been characterised.

For methods of identification as alkyl mercuric halides *see* *J.A.C.S.*, **47**, 3009 (1925), **50**, 167 (1928).

Other Reagents

Potassium 3-nitrophthalimide.
P. P. T. Sah and T. S. Ma. *Ber.*, **65**, 1630 (1932) ; *Sci. Rep. Nat. Tsing Hua Univ.*, **2**, 147 (1933).

Potassium phthalimide.
S. Gabriel. Various papers in *Ber.*, 1887 to 1902.

Potassium tetrachlorophthalimide.
C. G. F. Allen and R. V. V. Nicholls, *J.A.C.S.*, **56**, 1409 (1934).

These derivatives of phthalimide do not provide convenient methods for the halides in that they require heating with the substance in sealed tubes at high temperatures.

HYDROCARBONS, AROMATIC

Selected Reagents

Phthalic anhydride.
Picric acid.
Styphnic acid.
1 : 3 : 5-Trinitrobenzene.

The identification of benzene and its homologues has of recent years been simplified by the use of phthalic anhydride for the formation of *o*-benzoyl benzoic acids. These have precise melting points and may be titrated with standard alkali. The isomeric xylenes, however, may not be differentiated with this reagent and for this purpose tetrachlorophthalic anhydride is highly satisfactory. A monograph on this reagent is not however included since the intermediate acid required for its manufacture is not available at the present time.

The condensed aromatic hydrocarbons, such as naphthalene, anthracene, fluorene, acenaphthene, phenanthrene, etc., may be readily identified by their picrates and styphnates. It should be borne in mind that the *solvent* used for the preparation of the derivative is of the utmost importance. Thus the picrates and styphnates of acenaphthene, phenanthrene and naphthalene may be crystallised unchanged from alcohol; anthracene picrate and styphnate, however, crystallise well from benzene but are decomposed by alcohol.

Fluorene picrate must be prepared in ether solution. The styphnate, however, may be prepared in glacial acetic acid solution.

1 : 3 : 5-Trinitrobenzene has value as a confirmatory reagent for the condensed nuclear hydrocarbons.

Other Reagent

Tetrachlorophthalic anhydride.
H. W. Underwood and W. L. Walsh. *J.A.C.S.*, **57**, 940 (1935).

MERCAPTANS

Selected Reagent

2 : 4-Dinitrochlorobenzene.

This reagent is well suited to the identification of mercaptans, for the derivatives are easily and rapidly prepared. Further, the mercaptides may be oxidised to sulphones, which also have sharp melting points. This is particularly useful when the melting points of the mercaptides fall close together. Thus the melting points of the *o*- and *p*-cresyl mercaptan derivatives with 2 : 4-dinitrochlorobenzene are 101 and 103° respectively while the corresponding sulphones melt at 155 and 190°

Other Reagents

3 : 5-Dinitrobenzoyl chloride, }
3-Nitrophthalic anhydride. }
E. Wertheim. *J.A.C.S.*, **51**, 3661 (1929).

The dinitrobenzoyl chloride derivatives have melting points which lie close together and they are lower than the corresponding alcohol derivatives. The melting points of the nitrophthalic anhydride derivatives are even closer, although they are considerably higher and may also be titrated. The melting points of these derivatives vary, however, with the rate of heating.

NITRILES

Selected Reagents

α-Naphthyl *iso*-thiocyanate.
Phenyl *iso*-thiocyanate.

The nitriles are generally hydrolysed quite readily to acids, and in the **aromatic** series this will at once provide one useful derivative. The reduction of nitriles to amines and preparation of the thioureas by means of the above reagents is of particular use in the **aliphatic** series. The α-naphthyl thioureas are rather more satisfactory derivatives than the phenyl compounds.

Other Reagents

Grignard reagents.
R. L. SHRINER and T. A. TURNER. *J.A.C.S.*, **52,** 1267 (1930).
Phloroglucinol.
H. P. HOWELLS and J. G. LITTLE. *J.A.C.S.*, **54,** 2451 (1932).
Thioglycollic acid.
F. E. CONDO *et al.* *J.A.C.S.*, **59,** 230 (1937).

These reagents involve somewhat lengthy procedures and, by reason of this disadvantage, have not received further consideration, except in the case of phloroglucinol, where poor yields were obtained.

PHENOLS

Selected Reagents

Acetic anhydride.
Benzoyl chloride.
Chloroacetic acid.
3 : 5-Dinitrobenzoyl chloride.
Diphenyl carbamyl chloride.
α-Naphthyl *iso*-cyanate.
p-Nitrobenzoyl chloride.
p-Nitrobenzyl bromide.
Phenyl *iso*-cyanate.
Picric acid.
p-Toluenesulphonyl chloride.
1 : 3 : 5-Trinitrobenzene.
p-Xenyl *iso*-cyanate.

In selecting a reagent for the identification of phenols probably the first choice would be chloroacetic acid. Derivatives are easily prepared and have the advantage that they can be titrated with standard alkali, thereby establishing the equivalent weight of the derivative. Furthermore, a comprehensive range of melting points is available; the reagent, however, is not applicable to the nitrophenols.

Frequently the simple monohydric phenols, e.g. cresols, chlorophenols, give low melting derivatives with benzoyl chloride, *p*-nitrobenzoyl chloride, *p*-nitrobenzyl bromide and *p*-toluenesulphonyl chloride. In the case of the last-named reagent this does not constitute a disadvantage, for the *p*-toluenesulphonyl esters are readily crystallised.

Certain of the above reagents, *viz.*, 3 : 5-dinitrobenzoyl chloride, *p*-nitrobenzoyl chloride and phenyl *iso*-cyanate, decompose readily in the presence of water. Under some circumstances this represents a disadvantage.

With a number of notable exceptions, e.g. the naphthols, picric acid and trinitrobenzene are not used for the characterisation of phenols.

Acetic anhydride is of very little use for the identification of phenols, for the majority of the derivatives are liquid. Its importance lies in its use for the quantitative determination of the hydroxyl group.

α-Naphthyl *iso*-cyanate is a good general reagent for the phenols, the nitrophenols in particular. It is to be preferred to the more commonly used phenyl *iso*-cyanate on account of its greater stability. There are but few derivatives of xenyl *iso*-cyanate cited, but their melting points are somewhat higher than the corresponding phenyl or α-naphthyl compounds.

Other Reagents

Benzenesulphonyl chloride.

2 : 4-Dinitrochlorobenzene.
R. W. Bost and F. Nicholson. *J.A.C.S.*, **57**, 2368 (1935).

β-Naphthyl *iso*-cyanate.
P. P. T. Sah. *Rec. trav. chim.*, **58**, 453 (1939).

Benzenesulphonyl chloride is used essentially for the separation of amines. As a reagent for phenols it is not as satisfactory as *p*-toluenesulphonyl chloride, for the derivatives obtained have lower melting points.

2 : 4-Dinitrochlorobenzene would appear to be a good reagent for phenols, but in many instances we obtained oily derivatives which were extremely difficult to purify.

The *iso*-cyanates all show some tendency to decompose on standing; β-naphthyl *iso*-cyanate, being a solid, decomposes more rapidly than the liquid *iso*-cyanates. For this reason the liquid *iso*-cyanates are to be preferred as reagents.

SULPHONAMIDES

Selected Reagent

Xanthydrol.

Although sulphonamides are usually considered to be themselves derivatives, e.g. in the identification of sulphonic acids or sulphonyl chlorides, circumstances are quite possible in which derivatives could profitably be made. Xanthydrol is very convenient for this purpose, the derivatives being easily prepared and purified.

SULPHONIC ACIDS

Selected Reagent

Benzyl *iso*-thiourea hydrochloride.

Benzyl *iso*-thiourea hydrochloride is easily the best reagent proposed for sulphonic acids to date. The derivatives are prepared with ease and crystallise readily. The reagent is unsuited to aminosulphonic acids as the derivatives decompose at or near the melting point.

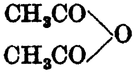
Other Reagents

Scattered throughout the literature there are numerous references to various amines being employed for the identification of sulphonic acids. Of these only the use of *p*-toluidine for the characterisation of phenanthrene sulphonic acids appears to be of special merit. Reference to this is made in the monograph on *p*-toluidine.

The classical method for identification of sulphonic acids is to convert them to the corresponding amides. By virtue of the fact that xanthydrol is a reagent for sulphonamides, it is suggested that the identity of the sulphonic acid might be confirmed by preparation of the xanthydrol derivative of the sulphonamide.

SELECTED REAGENTS

ACETIC ANHYDRIDE



$$\begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\Big> O$$

Mol. Wt. 102·0

Reagent for Alcohols, Phenols, Primary and Secondary Aromatic Amines

Acetic anhydride is a colourless liquid with a pungent odour, boiling at 137–140°. It dissolves in water slowly with the formation of acetic acid ; it is readily soluble in alcohol and in ether. Acetic acid, acetyl chloride, acetic anhydride and thioacetic acid have all been employed for the preparation of acetyl derivatives, but generally speaking the best results are obtained with acetic anhydride.

ALCOHOLS AND PHENOLS

A variety of methods has been suggested for the acetylation of phenols. These involve shaking a cold aqueous suspension of the phenol with acetic anhydride [12], refluxing the phenol with the reagent alone or in the presence of anhydrous sodium acetate [1], or in the presence of some catalyst such as sulphuric acid [2] or zinc chloride [3]. The condensation between acetic anhydride and phenols may be effected in the presence of an inert basic solvent such as pyridine or dimethylaniline [8].

The reagent is not advocated for the identification of alcohols and phenols for the majority of the derivatives are liquid. A number of melting points of the phenol derivatives will be found on reference to page 155 ; these compounds may be obtained by one of the above procedures. The reagent is warmly recommended, however, for the quantitative determination of alcohols and phenols.

Estimation of Hydroxy Compounds [8]

An acetylating solution is prepared by dissolving 120 g. acetic anhydride in 880 ml. pyridine. To 25 ml. of this solution, accurately measured, is added about 1 g., accurately weighed, of the hydroxy compound. The solution, in a flask fitted with reflux condenser, is heated on a water bath for an hour. For certain substances which do not acetylate easily it is necessary to prolong the time of refluxing. An equal volume of water is added to the cooled solution, which is then titrated with standard sodium hydroxide (N/1) using phenol phthalein as indicator. A blank titration is made at the same time and the difference between the two titrations represents a measure of the acetic anhydride required for acetylation.

For estimating the acetylisable constituents of essential oils, a method has been proposed whereby the acetate is isolated, purified and then saponified [11]. The amount of alkali used in the hydrolysis is a measure of the acetylisable constituents of the oil. For details of this method the reader is referred to the literature.

AMINES

Acetic anhydride is the classical reagent for the identification of aromatic primary and secondary amines. The aliphatic amines give rise to liquid derivatives.

$$R\cdot NH_2 + (CH_3CO)_2O \longrightarrow RNH\cdot OC\cdot CH_3 + CH_3COOH$$
$$RR'NH + (CH_3CO)_2O \longrightarrow RR'N\cdot OC\cdot CH_3 + CH_3COOH$$

Preparation of Derivatives

Dissolve the primary or secondary amine in glacial acetic acid, add an excess of acetic anhydride and reflux for a quarter of an hour. When acetylating secondary amines it is advisable to prolong the heating. Cool and pour the solution into water when the acetyl compound separates. Filter off, wash well with dilute acid and water and recrystallise from water or from aqueous alcohol.

For melting points of derivatives of

(*a*) primary aromatic amines, *see* page 129.

(*b*) secondary aromatic amines, *see* page 136.

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12. F. D. Chattaway. *J.C.S.*, 2495 (1931).

ANILINE

$C_6H_5NH_2$

Mol. Wt. 93·1

Reagent for Carboxylic Acids

Aniline is a clear oily liquid, almost colourless when freshly distilled, darkening to a reddish brown colour on keeping. It boils at 182–184°. Aniline will react directly with carboxylic acids to form anilides but it is more general first to convert the acid to the acid chloride and treat the latter with aniline.

$$R \cdot COOH + C_6H_5NH_2 \longrightarrow C_6H_5NH \cdot OC \cdot R + H_2O$$
$$R \cdot COCl + C_6H_5NH_2 \longrightarrow C_6H_5NH \cdot OC \cdot R + HCl$$

Preparation of Derivative [1]

Heat 1 g. of acid in a test tube with a slight excess of thionyl chloride to 100–120° for half an hour. Cautiously add an equivalent of aniline and heat to a somewhat higher temperature for half an hour. Recrystallise the product from alcohol or petroleum ether containing a little benzene.

For melting points of derivatives, *see* page 110.

OTHER APPLICATIONS

The reagent can be employed for the identification of acid chlorides, acid anhydrides and for the identification of the acid component of esters.

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P. W. Robertson. *J.C.S.*, **115**, 1210 (1919).

BENZALDEHYDE

C_6H_5CHO

Mol. Wt. 106·1

Reagent for Ketomethylenes, Primary Aromatic Amines and Phenylacetonitrile

Benzaldehyde is an almond smelling colourless liquid of boiling point 179°, undergoing oxidation to benzoic acid if allowed to remain exposed to air for long periods. A very reactive compound, its chief analytical use lies in the preparation of crystalline condensation products with compounds containing the ketomethylene group, e.g. acetone, acetophenone, and also with primary aromatic amines such as aniline, benzidine, etc.

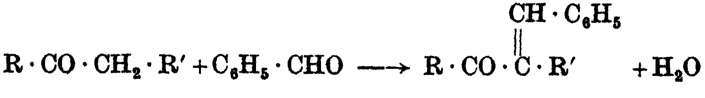
It is especially useful in differentiating between benzidine and *o*-tolidine (both compounds of M.P. 128°) since the melting points of their acetyl derivatives lie within 3° of each other.

KETOMETHYLENES

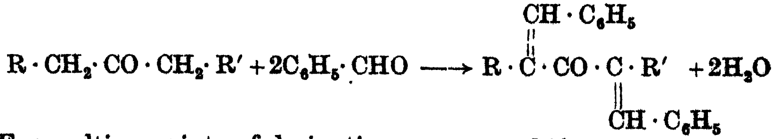
Preparation of Derivatives

Dissolve one molecular proportion of the ketomethylene compound and slightly more than one or two molecular proportions of benzaldehyde (depending on whether the ketomethylene compound is $R \cdot CH_2CO \cdot R'$ or $R \cdot CH_2COCH_2 \cdot R'$) in a little absolute alcohol. If about 1 g. of the ketomethylene compound is used, a suitable quantity of alcohol is 10 ml. Add 0·5 ml. 5N sodium hydroxide and allow the whole to stand for an hour or more at room temperature. The arylidene derivative usually crystallises out or will do so on scratching and after washing with a little cold alcohol can be recrystallised from absolute alcohol.

The reaction may be expressed as

(*a*)


$$R \cdot CO \cdot CH_2 \cdot R' + C_6H_5 \cdot CHO \longrightarrow R \cdot CO \cdot \overset{CH \cdot C_6H_5}{\overset{\|}{C}} \cdot R' \quad + H_2O$$

(*b*)


$$R \cdot CH_2 \cdot CO \cdot CH_2 \cdot R' + 2C_6H_5 \cdot CHO \longrightarrow R \cdot \overset{CH \cdot C_6H_5}{\overset{\|}{C}} \cdot CO \cdot \underset{CH \cdot C_6H_5}{\underset{\|}{C}} \cdot R' \quad + 2H_2O$$

For melting points of derivatives, *see* page 146.

AMINES

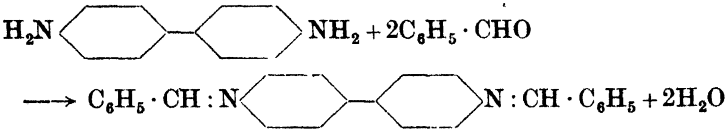
Preparation of Derivatives

The characterisation of primary aromatic amines is effected by warming the amine with one or two mols of benzaldehyde (depending on whether the base is a monoamine or diamine) either diluted with a suitable solvent such as alcohol or acetic acid, or without any diluent. The reaction is usually complete within 10 minutes and the anil may be recrystallised from alcohol or benzene.

The reaction occurs as follows :

(*a*) $ArNH_2 + C_6H_5 \cdot CHO \longrightarrow ArN:CH \cdot C_6H_5 + H_2O$

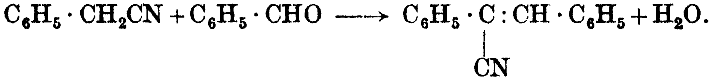
or (*b*)



For melting points of derivatives, *see* page 129.

Preparation of a Phenylacetonitrile Derivative

Owing to the reactivity of the methylene hydrogen atoms, phenylacetonitrile condenses very easily with benzaldehyde :



$$C_6H_5 \cdot CH_2CN + C_6H_5 \cdot CHO \longrightarrow C_6H_5 \cdot \underset{\displaystyle CN}{\underset{|}{C}} : CH \cdot C_6H_5 + H_2O.$$

Mix 2 ml. phenylacetonitrile with 2 ml. benzaldehyde and 2 ml. absolute alcohol. Add a few drops of 5N sodium hydroxide, stopper and shake hard. The solution becomes warm and after a few minutes crystals of the benzal compound (α-phenylcinnamonitrile) separate. After standing for 30 minutes dilute with water, collect the solid and wash with water followed by a *little* cold methyl alcohol. Recrystallise from methyl alcohol to obtain colourless needles of M.P. 86°.

BENZENESULPHONYL CHLORIDE

$C_6H_5 \cdot SO_2Cl$

Mol. Wt. 176·6

Reagent for Primary and Secondary Amines

Benzenesulphonyl chloride is a colourless or yellow liquid which solidifies at 14–15°.

When a primary amine is shaken with benzenesulphonyl chloride and excess sodium hydroxide a water soluble sodium salt results :

$$RNH_2 + C_6H_5 \cdot SO_2Cl + 2NaOH \longrightarrow RNNaSO_2 \cdot C_6H_5 + NaCl + 2H_2O$$

With secondary amines a water insoluble substituted amine is formed :

$$RR'NH + C_6H_5 \cdot SO_2Cl + NaOH \longrightarrow RR'NSO_2 \cdot C_6H_5 + NaCl + H_2O,$$

while tertiary amines do not react. When recrystallised the sulphonamides serve as useful derivatives for the characterisation of amines, and furthermore the original amine may be obtained by heating the sulphonamide in a sealed tube with concentrated hydrochloric acid at 140°.

The application of these reactions to the quantitative separation of amines was rendered more involved by Ssolonina's discovery [6] that certain primary amines gave disulphonyl derivatives :

$$RNH_2 + 2C_6H_5SO_2Cl \longrightarrow RN(SO_2C_6H_5)_2 + 2HCl$$

As these disulphonyl compounds are insoluble in alkalis they are liable to be confused with the monosulphonyl derivatives of secondary amines. Consequently a modified procedure was introduced by Hinsberg [12].

Separation of Primary, Secondary and Tertiary Amines

To 1 g. of amine or amine mixture add 20 ml. 12 per cent. sodium hydroxide solution and then in small portions, with shaking, 2·5 g. benzenesulphonyl chloride. Warm to remove the last traces of acid chloride. Acidify the alkaline solution with dilute hydrochloric acid when the sulphonamides of primary and secondary amines are precipitated, while any tertiary amine remains in solution as hydrochloride. Separate the solid. To convert any disulphonamide, that may have been formed from a primary amine, into the desired mono derivative, boil the solid under reflux with 0·8 g. sodium dissolved in 20 ml. alcohol. Then proceed as under (i) or (ii).

(i) *Amines containing less than seven carbon atoms.*

Dilute with water and evaporate off the alcohol; any secondary amine sulphonamide precipitates. Separate any solid and acidify the filtrate with dilute hydrochloric acid to precipitate any mono derivative of primary amine.

(ii) *Aliphatic and hydrocylic amines containing more than six carbon atoms.*

When the primary amine in the mixture has a comparatively high molecular weight, the separation by method (i) is not satisfactory owing to the sparing solubility of the sodium salt of the primary sulphonamide. In this case the following alternative procedure should be adopted.

Dilute the alcoholic solution with water and evaporate off the alcohol. Acidify and filter off the mixture of sulphonamides. Dissolve the dry solid in anhydrous ether and add small pieces of sodium or sodium wire to the ethereal solution and reflux gently for six to eight hours. Some unchanged sodium should be present at the end of this time. Cool, separate the solid mixture of the sodium salt of the primary amine sulphonamide and sodium, and wash the solid several times with small quantities of ether. Evaporate the solid with alcohol, dilute with water, and acidify to obtain the primary amine sulphonamide. Evaporate the ethereal solution to obtain the secondary amine sulphonamide.

The sulphonamides can be recrystallised from aqueous alcohol or from alcohol.

For melting point of derivatives of

(*a*) primary aromatic amines, *see* page 129.
(*b*) primary aliphatic amines, *see* page 127.
(*c*) secondary amines, *see* page 136.

OTHER APPLICATIONS

The reagent has also been employed for the identification of amino acids [2, 7, 8] and phenols [3].

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BENZOYL CHLORIDE

$C_6H_5 \cdot COCl$

Mol. Wt. 140·6

Reagent for Phenols and Primary and Secondary Amines

Benzoyl chloride is an almost colourless liquid which fumes in moist air. Benzoic anhydride has also been employed for the preparation of benzoyl derivatives, but it is necessary to heat the compound several hours with benzoic anhydride in the presence of sodium benzoate.

A number of procedures have been described for the preparation of benzoyl derivatives, but the method due to Schotten and Baumann, described below, is the one most widely used [1, 2]. The condensation may be brought about in the presence of sodium carbonate [4]; it may also be effected in pyridine, quinoline or dimethylaniline [6, 7] or in ethereal or in benzene solution in the presence of dry potassium carbonate [5]. Alternatively, derivatives may be prepared by refluxing the compound under test with the reagent.

$$C_6H_5COCl + ROH \longrightarrow C_6H_5COOR + HCl$$
$$C_6H_5COCl + RNH_2 \longrightarrow C_6H_5CONHR + HCl$$
$$C_6H_5COCl + RR'NH \longrightarrow C_6H_5CONRR' + HCl$$

Preparation of Derivatives

The phenol or amine is dissolved or suspended in 10 per cent. sodium hydroxide solution and an excess of benzoyl chloride is added in portions with shaking. The mixture is shaken vigorously until the odour of benzoyl chloride no longer persists. If the solution becomes warm it is advisable to cool under the tap. The solid is filtered off, washed well with water and recrystallised from alcohol or benzene.

For melting points of derivatives of

(*a*) primary aromatic amines, *see* page 129.
(*b*) primary aliphatic amines, *see* page 127.
(*c*) phenols, *see* page 155.

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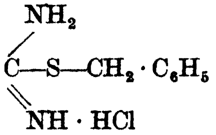
BENZYL-*iso*-THIOUREA HYDROCHLORIDE

(S-Benzylthiuronium Chloride)

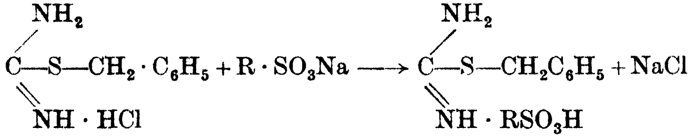


$$\mathrm{NH_2{-}C({=}NH\cdot HCl){-}S{-}CH_2\cdot C_6H_5}$$

Mol. Wt. 202·7

Reagent for Sulphonic Acids

Benzyl *iso*-thiourea hydrochloride is a white crystalline compound exhibiting dimorphism. The melting point may be 150–151° or 176–177°; both forms, however, yield the same derivatives with acids. The reagent was originally employed for the identification of carboxylic acids [1, 2, 3] but it finds a more important application in the characterisation of sulphonic acids. The amino-sulphonic acids provide the only exception to this statement, for the derivatives obtained from these acids invariably decompose on melting.



$$\overset{NH_2}{\underset{NH\cdot HCl}{C}}\text{—}S\text{—}CH_2\cdot C_6H_5 + R\cdot SO_3Na \longrightarrow \overset{NH_2}{\underset{NH\cdot RSO_3H}{C}}\text{—}S\text{—}CH_2C_6H_5 + NaCl$$

Preparation of Derivatives [4, 5]

Dissolve the sulphonic acid in 2N caustic soda and neutralise the excess base with hydrochloric acid. Add a strong aqueous solution of the reagent and cool in an ice bath. Recrystallise the solid which separates from 50 per cent. alcohol.

For melting points of sulphonic acid derivatives, *see* page 162.

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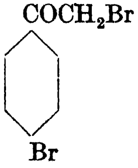
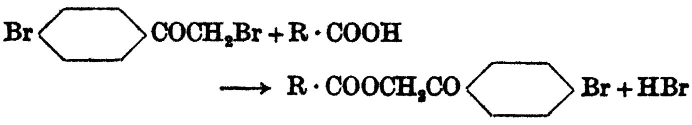
p-BROMOPHENACYL BROMIDE



Mol. Wt. 278·0

Reagent for Carboxylic Acids

The reagent is a white crystalline solid, melting at 106–108° C., insoluble in water, soluble in alcohol. The compound has similar uses to phenacyl bromide and it has the advantage of possessing better keeping qualities. *p*-Bromophenacyl bromide is extremely useful for the identification of carboxylic acids.



Preparation of Derivatives [1]

Dissolve 1 g. *p*-bromophenacyl bromide in 10 ml. alcohol and add this solution to the sodium salt of the acid in 5 ml. water. If solution is not complete on heating to boiling add more alcohol. Reflux for one, two or three hours according to whether the acid is mono-, di- or tri- basic and then cool. Filter off the derivative and recrystallise from alcohol or from aqueous alcohol.

For melting points of derivatives, *see* page 110.

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CHLOROACETIC ACID

$ClCH_2COOH$

Mol. Wt. 94·5

Reagent for Phenols

Chloroacetic acid is a white crystalline solid, melting at 61–63° and is extremely soluble in water. It condenses with phenols giving aryloxyacetic acids of definite melting points which are suitable for the identification of the phenols.

$$R \cdot OH + ClCH_2 \cdot COOH \longrightarrow R \cdot O \cdot CH_2 \cdot COOH + HCl$$

The derivative, being an acid, can be dissolved in alcohol-water mixture and titrated with standard alkali ; thus the equivalent weight of the derivative may be determined, thereby obtaining further confirmation of the identity of the phenol. The reagent is not suited to the identification of nitrophenols.

Preparation of Derivatives [2]

Dissolve or suspend 1 g. of the phenol in 3·5 ml. 33 per cent. caustic soda solution and to this add 2·5 ml. of a 50 per cent.

chloroacetic acid solution. If necessary a little water is added to dissolve the sodium phenate. Cork the test tube loosely and heat on a water bath for an hour. After cooling, just acidify to congo red with hydrochloric acid and extract with ether. Wash the ethereal solution once with water and then extract with sodium carbonate solution. Acidify the alkaline extract and recrystallise the resulting aryloxyacetic acid from water.

For melting point of derivatives, *see* page 155.

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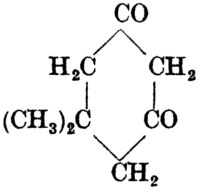
DIMEDONE

(5 : 5-Dimethylcyclohexane-1 : 3-dione)

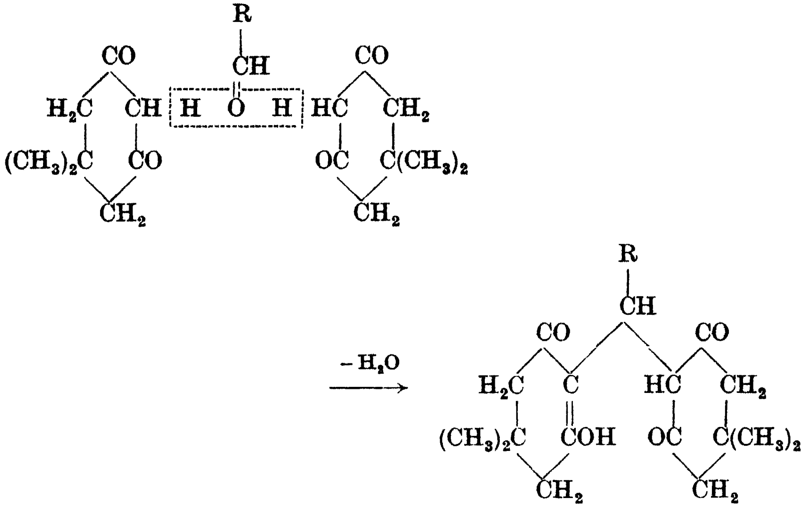


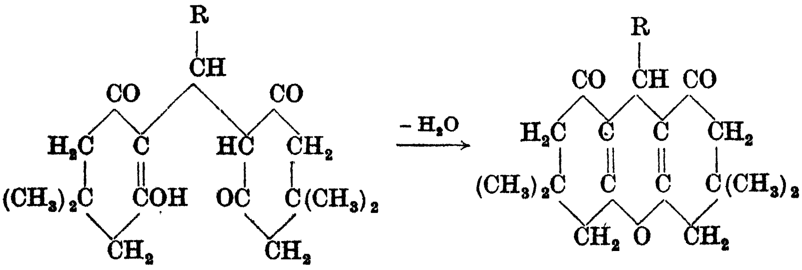
Mol. Wt. 140·2

Reagent for Aldehydes

Dimedone is a white crystalline substance melting at 147°. It is sparingly soluble in cold water (0·4 g. in 100 ml. at 19°) but appreciably more soluble at higher temperatures (3·8 g. per 100 ml. at 90°), while alcohol dissolves the substance fairly freely.

Aldehydes enter into combination with dimedone according to the equation shown. Ketones react only under exceptional conditions, so that the reagent may be regarded as specific for aldehydes. The condensation takes place in neutral, dilute acid or alkaline solution, and with some exceptions, the derivatives are obtained in well-crystallised form. Their melting points offer convenient means of characterisation while, in the cases of formaldehyde and acetaldehyde, the reaction with dimedone has formed the basis of methods of determination. These methods are based firstly on the very low water solubility of the methylene and ethylidene compounds, and secondly on the acidic properties arising from their enolic constitution, which permit of alkalimetric titration. The derivatives as a class are soluble in dilute alkali and their dilute alcoholic solutions yield colours with ferric chloride solution. These properties disappear if the enolic compounds are heated with certain reagents, such as acetic acid, acetic anhydride or absolute alcohol, the change being attributed to ring closure with loss of one molecule of water [3].





These products of dehydration were termed ‘ anhydrides ’ by Vorländer who determined melting points for a number of them.

Preparation of Derivatives

The derivatives of water-soluble aldehydes may be precipitated under neutral or slightly acid conditions with a warm aqueous solution containing two molecular equivalents of dimedone, but more commonly it is necessary to use dilute alcohol as solvent. For example—0·2 g. of heptaldehyde is added to a solution of 0·6 g. of dimedone in 30 ml. of 50 per cent. alcohol. The solution is warmed and then allowed to stand 2 to 3 hours when the derivative separates in glistening crystals which may be recrystallised from dilute alcohol. The use of undiluted alcohol is not recommended either for the condensation or the recrystallisation since it has the effect of causing ring closure with some derivatives. Mineral acids may have a similar effect. Certain derivatives, e.g. those of acrolein and furfural, often separate as precipitates of colloidal appearance. Vigorous shaking coagulates such precipitates quite readily.

Preparation of ' Anhydrides '

The ease with which the ' anhydrides ' are formed varies greatly. For example, the enol derivative of formaldehyde must be warmed with concentrated sulphuric acid or acetic anhydride, while the derivatives of acetaldehyde, propionaldehyde and *iso*-valeraldehyde are converted by dilute mineral acid or by heating with acetic acid. Others were treated by Vorländer with hot acetic acid for periods up to 20 hours. The absence of any reasonably general directions for preparation of the ' anhydrides ' detracts from their utility but such melting points as are available are quoted in the appropriate table. For the simple aliphatic aldehydes up to C_7, with the exception of formaldehyde, the following procedure has been found satisfactory. One-tenth to 0·2 g. of the enol, or equivalent quantities of the aldehyde and dimedone, are heated in a water bath with 10 ml. N/1 hydrochloric acid and sufficient alcohol (10–20 ml.) added to complete solution. The ' anhydride ' crystallises on cooling or is precipitated by the addition of water. It is shaken with dilute sodium hydroxide solution to remove any enol compound and recrystallised from dilute alcohol.

For melting points of derivatives, *see* page 120.

Quantitative Methods [4, 7, 10, 11]

An aqueous solution of formaldehyde containing only 0·004 per cent. of the aldehyde will yield a precipitate within 10 to 20 minutes when treated with an aqueous solution of dimedone in excess, and it is claimed [11] that when the methylene derivative is precipitated with excess dimedone from a solution buffered with sodium acetate and hydrochloride acid at pH 4·6 quantitative results of a high order of accuracy are obtained. Twelve hours is the minimum time recommended for complete precipitation and after drying at 60° the derivative is weighed. The fact that the precipitate weighs nearly ten times as much as the formaldehyde from which it is derived contributes considerably to the precision of the method, particularly as applied to small quantities of the aldehyde. The formaldehyde derivative may also be titrated in alcoholic solution as a monobasic acid. (Other aldehydes yield derivatives which are monobasic or dibasic according to the temperature or solvent.)

If acetaldehyde is also present it can interfere in the gravimetric method since its dimedone derivative is only slightly soluble though more soluble than that of formaldehyde. Vorländer [4] has devised a method of separation whereby the ethylidene derivative is converted to 'anhydride' by heating the mixture for 6–7 hours with acetic acid at 100°. After precipitation with water the formaldehyde derivative may then be extracted with dilute sodium hydroxide and reprecipitated with acetic acid. This, and three other methods of dealing with formaldehyde acetaldehyde mixtures, are claimed to yield approximately quantitative results [4].

The dimedone derivative of propionaldehyde is also very sparingly soluble in water.

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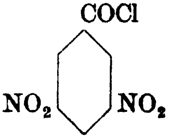
3 : 5-DINITROBENZOYL CHLORIDE



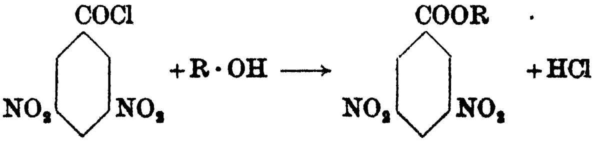
Mol. Wt. 230·6

Reagent for Alcohols and Phenols

3 : 5-Dinitrobenzoyl chloride is a white crystalline solid of melting point 68–69°, which hydrolyses in moist air to dinitrobenzoic acid and hydrochloric acid. The reagent is soluble in non-hydroxylic solvents without decomposition.

ALCOHOLS [2, 3, 7, 11]

The reagent is particularly recommended for the identification of alcohols, for although the 3 : 5-dinitrobenzoic esters melt somewhat low they crystallise easily and readily. Furthermore, the esters form addition compounds with α-naphthylamine. The addition compounds have definite melting points which are, almost without exception, much higher than those of the original esters and which further serve to define the alcohol under test.



Preparation of Derivatives [2]

Add 1 g. of the dinitrobenzoyl chloride dissolved in 10 ml. benzene to the alcohol under test and then add a few ml. of anhydrous pyridine. Heat to boiling, cool and add ether in excess. In the case of tertiary alcohols it is necessary to reflux for 30 minutes.

Wash the ethereal solution with dilute acid, followed by dilute alkali and then with water. Evaporate the ethereal solution to dryness and recrystallise the solid from petroleum ether or benzene, or alternatively, add an excess of α-naphthylamine dissolved in ether to the ethereal solution and recrystallise the resulting solid from alcohol.

For melting points of derivatives, *see* page 115.

PHENOLS [1, 6]

Preparation of Derivatives [6]

Dissolve 1 g. of the phenol in 20 ml. pyridine and add 2·5 g. reagent. Reflux for one hour, cool and pour into 400 ml. cold 5 per cent. *v/v* sulphuric acid solution. Wash the solid with water and introduce it into 200 ml. 2 per cent. sodium hydroxide solution, filter and wash with water. In the event of an oil separating on pouring into dilute sulphuric acid, extract the oil with ether, wash the ethereal solution with sodium hydroxide solution and with water and evaporate to dryness. Recrystallise the crude derivative from alcohol.

For melting points of derivatives, *see* page 155.

OTHER APPLICATIONS

The reagent has been employed for the characterisation of mercaptans [4]. The melting points of the derivatives lie close together and the reagent is therefore not well suited for this purpose.

Ethers [5] can be identified with 3 : 5-dinitrobenzoyl chloride. The reagent is condensed with the ether in the presence of zinc chloride yielding esters; its application is limited, however, to symmetrical ethers.

Finally, the reagent has been employed for a wide range of amino acids [8, 9, 10]. Slight variations in the method of preparing derivatives of the individual amino acids are described and there appear to be slight discrepancies in melting points of certain derivatives. For these reasons the reader is advised to refer to the literature for details of preparation of the dinitrobenzoates of the various amino acids.

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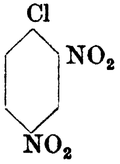
2 : 4-DINITROCHLOROBENZENE



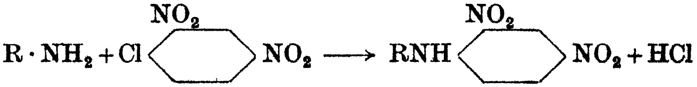
Mol. Wt. 203·6

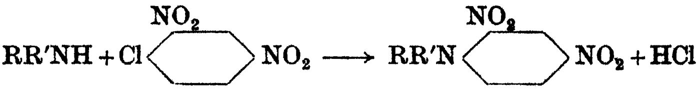
Reagent for Primary and Secondary Amines and for Mercaptans

The reagent is a yellow crystalline solid melting at 50°. It is insoluble in water, sparingly soluble in cold alcohol but readily soluble in hot alcohol.

AMINES

2 : 4-Dinitrochlorobenzene is a most satisfactory reagent for the identification of primary and secondary, aliphatic and aromatic amines. The reaction is represented by the following equations :





Preparation of Derivatives [1, 2, 3, 4, 5, 6]

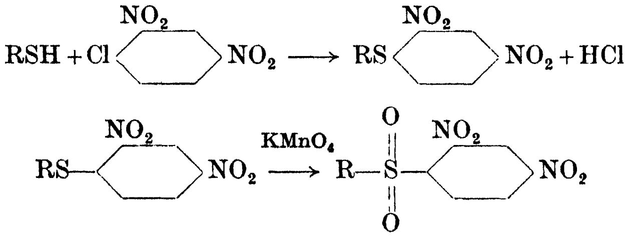
Equivalent quantities of the reagent and amine are heated together on a water bath for some minutes and the product is recrystallised from alcohol.

For melting points of derivatives of

(*a*) primary aromatic amines, *see* page 129.
(*b*) primary aliphatic amines, *see* page 127.
(*c*) secondary amines, *see* page 136.

MERCAPTANS

2 : 4-Dinitrochlorobenzene readily forms derivatives with mercaptans and is particularly suitable for the identification of these compounds. The mercaptides which are formed have definite melting points, as have the sulphones which can readily be obtained by oxidation of the mercaptides. This is a decided advantage when the melting points of two mercaptides lie close together.



Preparation of Derivatives [7, 8]

(a) Mercaptides

Dissolve about 1 g. of the mercaptan in 30 ml. of alcohol, or in the minimum amount necessary for solution and add 0·4 g. sodium hydroxide in 3 ml. water. Add this solution to 2 g. of the reagent in 10 ml. alcohol and heat the solution on a steam bath for ten minutes. Filter the hot solution, and recrystallise the mercaptide, which separates on cooling, from alcohol.

(b) Sulphones

Dissolve the mercaptide in the minimum quantity of acetic acid, warming if necessary, and treat with a 50 per cent. excess of potassium permanganate dissolved in thirty times its weight of water. Some mercaptides tend to precipitate, in which case add more acetic acid. Pass in the minimum amount of sulphur dioxide to remove the excess permanganate and add ice. Filter off the sulphone and recrystallise from alcohol.

For melting points of derivatives, *see* page 152.

Other Applications

2 : 4-Dinitrochlorobenzene has been employed for the characterisation of phenols [9] but it is our experience that the reagent is unsatisfactory for this purpose. We found that frequently the derivatives were oils and difficult to purify.

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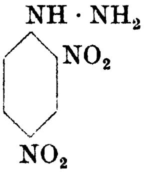
2 : 4-DINITROPHENYLHYDRAZINE



Mol. Wt. 198·1

Reagent for Aldehydes and Ketones

2 : 4-Dinitrophenylhydrazine is a red crystalline solid melting at 195–196°, insoluble in water and only slightly soluble in cold organic solvents.

Its special use has been in providing derivatives of the lower aldehydes and ketones, the use of phenylhydrazine or hydroxylamine giving rise to oils or low-melting solids. The yield of derivative obtained is usually high and in some cases, using defined conditions, can be made quantitative, enabling the estimation of the carbonyl compound to be achieved.

Campbell [27] found the melting points of many derivatives given in the literature to be in error and made a thorough investigation of the problem.

Detection of Carbonyl Compounds

Shake the suspected aldehyde or ketone with a saturated aqueous solution of 2 : 4-dinitrophenylhydrazine hydrochloride (1 to 2 g. per litre), warming if necessary. A yellow or red precipitate indicates the presence of the carbonyl group.

Preparation of Derivatives

Dissolve 0·5 g. 2 : 4-dinitrophenylhydrazine in 1 ml. warm concentrated sulphuric acid and dilute with 5 to 10 ml. absolute alcohol. At once add the aldehyde or ketone dissolved in absolute alcohol. The dinitrophenylhydrazone usually separates at once or on cooling, but in some cases boiling for a few minutes is necessary. The crystals are collected, washed with a little absolute alcohol, and recrystallised from a suitable solvent (usually alcohol, glacial acetic acid, xylene or nitrobenzene).

Generally the derivatives from aldehydes and ketones of the saturated aliphatic series are soluble in hot alcohol and are yellow or orange in colour. Those from benzaldehyde and its simple substitution products are not soluble in alcohol and are red, orange or yellow. Dinitrophenylhydrazones derived from $\alpha : \beta$ unsaturated carbonyl compounds are usually red.

For melting points of derivatives of

(*a*) aldehydes, *see* page 120.
(*b*) ketones, *see* page 146.

Determination of Carbonyl Compounds

The procedure adopted by Iddles and his co-workers [22, 33] is to add an aqueous or alcoholic solution of the carbonyl compound to an excess of a saturated solution of dinitrophenylhydrazine in 2N hydrochloric acid at 0°, and allow to digest for 1 to 24 hours at that temperature. The precipitate is collected, washed with the acid reagent solution and finally with water until free chloride. The solid is then dried *in vacuo* or at 100–110°, to constant weight.

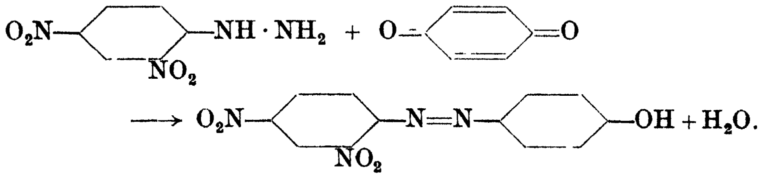
By this method acetaldehyde, acetone, methyl ethyl ketone, methyl *n*-propyl ketone, benzaldehyde, *p*-hydroxybenzaldehyde, salicylaldehyde, *o*-methoxybenzaldehyde, vanillin (all in aqueous solution), acetophenone, benzoin, mesityl oxide, benzalacetophenone, benzil; benzophenone, piperonal, cyclohexanone, cyclopentanone, and carvone (these from alcoholic solution) have been determined with recoveries of from 93 to 103 per cent.

By similar methods ascorbic acid [37], santonin [11], hexetone (6-*m*-menthene-5-one) [17], camphor [10, 21, 28, 32, 34], menthone [10], furfural [10, 15, 18, 23], formaldehyde [19], and cinnamaldehyde [19, 35] have also been estimated.

Small amounts of aldoximes may be determined by adding a weighed amount to a solution of dinitrophenylhydrazine in 2N hydrochloric acid and standing for several hours. The resulting dinitrophenylhydrazone is collected, dried and weighed [6].

Reaction with *p*-Quinones

Borsche [3] has shown that 2 : 4-dinitrophenylhydrazine reacts abnormally with *p*-benzoquinone as follows :



The condensation is effected by mixing hot alcoholic solutions of dinitrophenylhydrazine hydrochloride and the quinone, allowing the mixture to cool and stand. The dinitro-azo-phenol separates from solution on dilution. Similar reactions are given by *p*-toluquinone and thymoquinone.

Polymorphism of Dinitrophenylhydrazones

Bredereck and Fritzsche [12, 31] have shown that the derivatives of some aldehydes of the furane and pyrrol rings exist in two modifications, yellow and red in colour.

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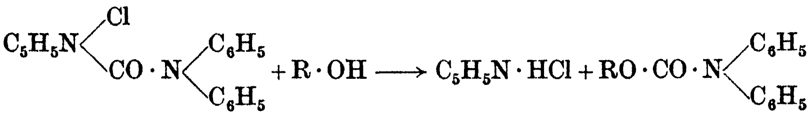
DIPHENYLCARBAMYL CHLORIDE

$(C_6H_5)_2N \cdot COCl$

Mol. Wt. 231·7

Reagent for Phenols

Diphenylcarbamyl chloride is a white to pale yellow crystalline solid melting at 85–86°. In presence of pyridine it forms esters with phenols, the esterification being preceded by the formation of a pyridine addition compound isolated by Herzog [3] who formulated the reaction as follows :



$$\mathrm{C_5H_5N}\begin{cases}\mathrm{Cl}\\ \mathrm{CO\cdot N}\begin{cases}\mathrm{C_6H_5}\\ \mathrm{C_6H_5}\end{cases}\end{cases} + \mathrm{R\cdot OH} \longrightarrow \mathrm{C_5H_5N\cdot HCl} + \mathrm{RO\cdot CO\cdot N}\begin{cases}\mathrm{C_6H_5}\\ \mathrm{C_6H_5}\end{cases}$$

The reagent is soluble in alcohol without ready esterification though this is said to take place slowly on standing, and quite easily in presence of alkali or potassium cyanide. The earlier work [1] on the reagent was concerned with rhodinol which forms an ester melting at 83–84°.

A free carboxyl group may prevent the condensation ; thus salicylic acid forms no derivative, but the rule is not general [3]. The number of melting points published is rather limited but those which are available show fairly good differentiation.

Preparation of Derivatives

One gram of the phenol is dissolved in 5 ml. pyridine with less than one equivalent of diphenylcarbamyl chloride. The mixture is refluxed for 30 minutes and then poured into cold water. A somewhat resinous mass is precipitated and, in exceptional cases, e.g. with resorcinol, may require to stand for some hours to solidify. The solid is separated from the water and recrystallised from alcohol. Petroleum ether, carbon tetrachloride and benzene have also been recommended as solvents.

For melting points of derivatives, *see* page 155.

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FORMIC ACID

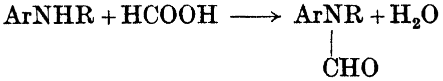
HCOOH

Mol. Wt. 46·0

Reagent for Primary and Secondary Aromatic Amines

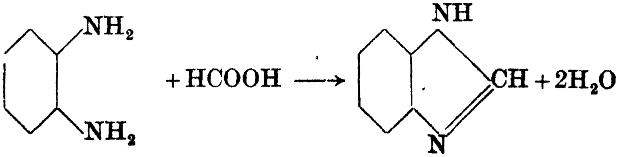
Formic acid is most conveniently used for analytical purposes as the commercially available 90 per cent. *w/w* solution.

The condensation products given with the above-mentioned classes of compounds are well crystallised and possess sharp melting points. The equation for the reaction is as follows :



$$\mathrm{ArNHR + HCOOH \longrightarrow Ar\underset{\displaystyle CHO}{\underset{|}{N}}R + H_2O}$$

It will characterise each of the three phenylene diamines. It should be noted, however, that the derivative obtained from *o*-phenylene diamine is benziminazole, viz. :



Preparation of Derivatives

The amine (0·5 g.) is refluxed for 10 minutes with 5 ml. 90 per cent. formic acid and the hot solution diluted with about 10 ml. cold water. The derivative, which separates either at once or on cooling in a freezing mixture followed in some cases by saturation with sodium chloride, is filtered off, washed with cold water and recrystallised from a suitable solvent (usually alcohol, water or, for the lower melting derivatives, petroleum ether of boiling point 60–80°).

Note that 2-amino-3-nitrotoluene forms *no* formyl derivative under these conditions owing to steric hindrance.

For melting points of derivatives, *see* pages 129 and 136.

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HYDROXYLAMINE HYDROCHLORIDE

$NH_2OH \cdot HCl$

Mol. Wt. 69·5

Reagent for Aldehydes and Ketones

This reagent occurs as colourless crystals readily soluble in water and in alcohol. With carbonyl compounds hydroxylamine hydrochloride reacts according to the following equation, forming oximes

$$RR'C:O + NH_2OH \cdot HCl \longrightarrow RR'C:NOH + H_2O + HCl$$

The oximes are employed for the characterisation of a number of carbonyl compounds, but as far as many of the lower members of this class are concerned the oximes are of rather low melting point, soluble to an inconvenient degree and difficult to purify. Consequently other reagents, such as semicarbazide hydrochloride, *p*-nitrophenylhydrazine or 2 : 4-dinitrophenylhydrazine, find more general application as means of identification.

The above reaction also forms the basis of a volumetric method for the determination of certain aldehydes and ketones. This method, which is of particular interest in the examination of essential oils, depends upon the fact that the hydrochloric acid set free in the process of oximation may be titrated with standard alkali.

Preparation of Derivatives

Aldehydes react readily in the cold when mixed with a solution of hydroxylamine hydrochloride in which the mineral acid has been neutralised with sodium acetate, sodium carbonate or sodium hydroxide. For example, 1 g. of an aliphatic aldehyde containing about seven carbon atoms is dissolved in 5 ml. alcohol and mixed with a solution of 1 g. hydroxylamine hydrochloride and 2 g.

sodium acetate in 3 ml. water. A little more alcohol is added if necessary to complete solution of the aldehyde and after standing for ½ to 1 hour the oxime is crystallised by cooling in ice. With aromatic aldehydes it is advantageous to employ an excess of sodium hydroxide, but this will need subsequent neutralisation in order to precipitate the oxime.

Ketoximes are not formed so readily as the aldoximes, and long standing or refluxing is generally necessary. The more vigorous conditions are required in the aromatic series, where an excess of hydroxylamine and a two- to three-fold excess of sodium hydroxide is commonly employed and the solvent must be mainly alcoholic.

In the preparation of alicyclic oximes Hückel and Sachs [7] have made good use of Ölander's results [6], which showed that oximation proceeds rapidly in solutions buffered with sodium acetate at pH 4·7. Hydroxylamine hydrochloride with no neutralising agent has been found suitable for the oximation of ketonic acids [3].

The oximes are isolated by neutralising any excess soda and dilution of alcoholic liquids with water. The more soluble oximes may be extracted with ether. For recrystallisation alcohol is employed.

α-Diketones form mono- and di-oximes, while β-diketones readily yield cyclic compounds. The possibility of stereoisomeric mixtures of oximes cannot always be disregarded. Fenchone yields a mixture which requires careful purification to yield the oxime melting at 167° [7], and in our own experience furil gives a mixture of the α- and β-stereoisomers which are not very readily separated.

The effect of steric hindrance on oxime formation is dealt with fully by Stewart [4].

For melting points of derivatives of

(*a*) aldehydes, *see* page 120.

(*b*) ketones, *see* page 146.

Quantitative Methods

The acid liberated in the course of the condensation is titrated under carefully controlled conditions. Standardised procedures designed for the examination of essential oils have been published by the Society of Public Analysts [8, 9].

The following method is applicable to aliphatic and many aromatic aldehydes and to aliphatic and alicyclic ketones, but aromatic ketones yield low results.

Dissolve 7 g. hydroxylamine hydrochloride in 100 ml. water, add 1 ml. bromophenol blue (0·04 per cent.) solution and titrate with N/1 sodium hydroxide to the blue colour of the indicator. Weigh accurately 3 to 5 g. of the aldehyde or ketone into a stoppered flask, add the solution of hydroxylamine and sufficient alcohol, if necessary, to dissolve the sample, shake and allow to stand one hour. Transfer to a 500 ml. stoppered flask (for convenient shaking), add 20 ml. petroleum ether (B.Pt. 60–80°) and titrate with N/1 sodium hydroxide, with vigorous shaking, until the indicator assumes the same blue colour as in the preliminary adjustment.

The use of a large proportion of alcohol renders the end point less distinct and in such a case it is desirable to prepare the original hydroxylamine solution with a similar concentration of alcohol and in sufficient quantity to reserve a portion as a colour standard. The alcohol should be free from aldehydes and ketones.

Modified volumetric methods, applicable to camphor, carvone, menthone, camphylene and other substances will be found under references [10, 11]. The liberation of acid from hydroxylamine hydrochloride has also been proposed as a sensitive test for carbonyl compounds, the reaction being carried out in the presence of a suitable pH indicator [12].

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METHYL IODIDE

CH_3I

Mol. Wt. 141·9

Reagent for Tertiary Amines

Methyl iodide, a colourless liquid of boiling point 42° which remains stable indefinitely if kept over a small amount of mercury, forms addition compounds with tertiary amines whether aliphatic, aromatic or heterocyclic. A few of the compounds obtained are difficult to isolate in the pure state and this difficulty may also be encountered when the base used is impure. In the majority of cases, however, both isolation and purification are simple. One great advantage that these derivatives possess is the fact that the iodine is fully ionised in aqueous solution and may be titrated with silver nitrate in neutral or acid solution. Since the compounds are all of the general formula 1 mol. base : 1 mol. methyl iodide, the titre immediately indicates the molecular weight of the tertiary amine.

Preparation of Derivatives

A mixture of 0·5 g. tertiary amine and 0·5 ml. methyl iodide is allowed to stand for 5 minutes. Whether spontaneous reaction has occurred or not, heat for a further 5 minutes in a water-bath and then cool in an ice-bath. The mixture should set solid, or if not, should do so on scratching with a glass rod. The product, which may be colourless or yellow, is recrystallised from a suitable solvent such as absolute alcohol, acetone, acetic acid or ethyl acetate.

For melting points of derivatives, *see* page 138.

a-NAPHTHYL *iso*-CYANATE

(*a*-Naphthyl Carbimide)

$C_{10}H_7 \cdot N:C:O$

Mol. Wt. 169·2

Reagent for Alcohols, Phenols, Primary and Secondary Amines and Halides

α-Naphthyl *iso*-cyanate is a colourless liquid of boiling point 153° at 18 mm. pressure. When heated its vapour is irritant, but this characteristic is far less pronounced than is the case with phenyl *iso*-cyanate. It is also considerably more stable towards water, a further advantage both in storage and in use.

ALCOHOLS AND PHENOLS

The reagent yields α-naphthylurethanes with alcohols and phenols by a reaction analogous to that undergone by phenyl *iso*-cyanate (page 75).

$$C_{10}H_7 \cdot N:C:O + R \cdot OH \longrightarrow C_{10}H_7 \cdot NH \cdot COOR$$

Preparation of Derivatives

The general method of preparation is similar to that described for the phenylurethanes (page 75) but absence of water is not essential when employing the α-naphthyl compound unless the alcohol or phenol is so unreactive that heating is necessary, in which case an undue proportion of di-α-naphthylurea may be formed. Secondary alcohols generally need heating with the reagent and the urethanes of tertiary alcohols are obtained with greater difficulty or not at all. It is recommended [3] to carry out the reaction in boiling petroleum ether (B.Pt. 100–120°) for cinnamyl alcohol, menthol, borneol, *iso*-borneol and benzoin. Certain phenols give difficulty, as for example *o*-nitrophenol and *o*-chlorophenol, but in these cases the addition to the reaction mixture of 2–3 drops of an ethereal solution of a tertiary amine, e.g., trimethylamine, induces an immediate reaction. The polyhydric phenols, resorcinol, quinol, catechol and pyrogallol do not yield α-naphthylurethanes [2]. The derivatives generally crystallise well from petroleum ether (B. Pt. 100–120°) but those of the polyhydric alcohols are best crystallised from ethyl alcohol after removing any excess *iso*-cyanate with ether or benzene.

For melting points of derivatives of

(*a*) alcohols, *see* page 115.

(*b*) phenols, *see* page 155.

AMINES

α-Naphthyl *iso*-cyanate reacts readily with primary and secondary amines both aliphatic and aromatic to form substituted ureas, but only a limited number of these derivatives have been prepared and characterised and these are mainly aliphatic [2].

$$C_{10}H_7NCO + R \cdot NH_2 \longrightarrow C_{10}H_7NH \cdot CO \cdot NHR$$

Preparation of Derivatives

The reaction is carried out by mixing the reactants in molecular proportions. The lower amines react very vigorously and, to avoid loss due to volatilisation, petroleum ether (B. Pt. 100–120°) is best employed as solvent. The same solvent may be used for crystallisation, but in some cases, e.g., methylamine and *o*-aminophenol, ethyl alcohol is to be preferred. The stability of the reagent towards water is again of considerable advantage since the gaseous lower amines are generally encountered in aqueous solution and such solutions may be treated quite satisfactorily for the preparation of these derivatives.

For melting points of amine derivatives, *see* pages 127 and 136.

HALIDES [6, 11]

α-Naphthyl *iso*-cyanate may be employed in precisely the same manner as phenyl *iso*-cyanate (page 76) for the characterisation of alkyl halides through the Grignard reaction. It is claimed [6] that the naphthalides so obtained are less soluble and better crystallised than the anilides but, while the melting points of the α-naphthalides lie in a more satisfactory range, fewer have been determined. Some aryl halides have been included (*see* table, page 142).

OTHER APPLICATIONS

The reagent has also been employed in the study of aminoacids and a limited number of derivatives have been prepared and characterised. On this subject reference should be made to the original literature [1, 2].

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α-NAPHTHYL *iso*-THIOCYANATE

$C_{10}H_7N:C:S$

Mol. Wt. 185·2

Reagent for Primary and Secondary Aliphatic Amines

α-Naphthyl *iso*-thiocyanate is a white crystalline substance of melting point 53–56°, insoluble in water but soluble in alcohol. Its reaction with amines is similar to that described for phenyl *iso*-thiocyanate (page 81) but with aliphatic amines the α-naphthyl

$$C_{10}H_7N:C:S + R\cdot NH_2 \longrightarrow C_{10}H_7NH\cdot CS\cdot NHR$$

thioureas show better characteristics for identification purposes, and melting points have also been determined for a number of secondary amine derivatives.

Preparation of Derivatives

Equivalent quantities of the reagent and the amine are dissolved in a small volume of alcohol. If no spontaneous reaction occurs the mixture is warmed and set aside to cool. The thioureas are recrystallised from alcohol or dilute alcohol and show a marked tendency to form supersaturated solutions.

For melting points of derivatives of
- (*a*) primary amines, *see* page 127.
- (*b*) secondary amines, *see* page 136.

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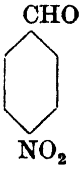
p-NITROBENZALDEHYDE



Mol. Wt. 151·1

Reagent for Primary Aromatic Amines

p-Nitrobenzaldehyde occurs as pale yellow needles melting at 106°, easily soluble in hot alcohol, insoluble in water. It forms condensation products with primary aromatic amines according to the equation

$$ArNH_2 + OHC \cdot C_6H_4 \cdot NO_2 \longrightarrow ArN:HC \cdot C_6H_4 \cdot NO_2 + H_2O$$

The condensation may be effected by refluxing the two components in alcoholic solution but reaction is much more rapid when glacial acetic acid is employed as the solvent. The condensation products, which are varying shades of yellow, are easily purified by recrystallisation and possess sharp melting points. The yield of derivative is excellent in the great majority of cases

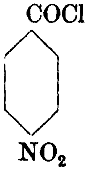
Preparation of Derivatives

A solution of 0·5 g. primary amine and one molecular proportion of the reagent in 5 ml. glacial acetic acid is refluxed for 30 minutes. The solid separating with or without careful dilution with water is filtered off and recrystallised from a suitable solvent, usually alcohol, glacial or dilute acetic acid.

The use of this procedure with the naphthylamines gives rise to a somewhat resinous product. For these derivatives the following method should be employed: Separately dissolve 0·5 g. amine and one molecular proportion of reagent in 10 ml. glacial acetic acid and mix the boiling solutions. Stir to mix thoroughly, allow to crystallise, filter off and recrystallise from glacial acetic acid.

For melting points of derivatives, *see* page 129.

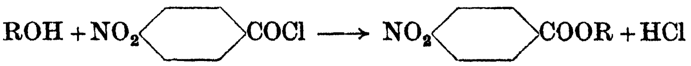
p-NITROBENZOYL CHLORIDE



Mol. Wt. 185·6

Reagent for Alcohols and Phenols

p-Nitrobenzoyl chloride is a pale yellow crystalline powder of melting point 72–73° which slowly hydrolyses in moist air to *p*-nitrobenzoic acid. The reagent is readily soluble in benzene and carbon tetrachloride but somewhat less soluble in petroleum ether. Alcohols and phenols rapidly yield *p*-nitrobenzoic esters with the reagent.



Preparation of Derivatives

Dissolve the alcohol or phenol in a small amount of pyridine and add an equivalent, or slight excess, of *p*-nitrobenzoyl chloride. After refluxing for a short time cool the solution and add water. Filter off the solid ester, wash with a little cold dilute sodium hydroxide and then with water. Recrystallise the alcohol derivatives from petroleum ether and the phenyl esters from alcohol.

For melting points of derivatives of

(*a*) alcohols, *see* page 115.
(*b*) phenols, *see* page 155.

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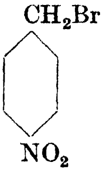
p-NITROBENZYL BROMIDE



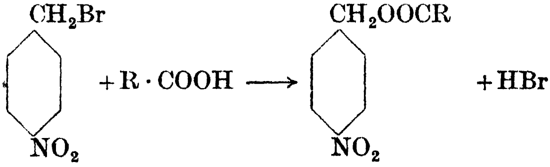
Mol. Wt. 216·0

Reagent for Carboxylic Acids, Substituted Barbituric Acids and Phenols

p-Nitrobenzyl bromide is a light-yellow feathery crystalline powder melting at 98–100°. The reagent, which is soluble in alcohol, is slightly lachrymatory. *p*-Nitrobenzyl chloride and iodide have also been proposed as reagents but the bromide is to be preferred because, in general, it reacts more readily than the chloride and is more soluble in alcohol than the iodide.

CARBOXYLIC ACIDS [1, 3, 4, 7]

With carboxylic acids the reagent gives rise to the corresponding *p*-nitrobenzyl esters.



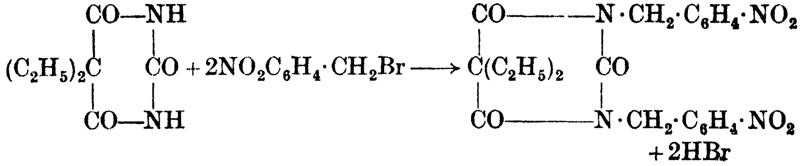
Preparation of Derivatives

Dissolve 1 g. of the sodium salt of the acid in 5 ml. water and add 1 g. of the reagent dissolved in 10 ml. alcohol. Reflux the solution one hour and cool. Crystallise the derivative which separates from alcohol or from aqueous alcohol. For polybasic acids it is advisable to extend the time of refluxing to two or three hours according to the basicity of the acid.

For melting points of derivatives, *see* page 110.

SUBSTITUTED BARBITURIC ACIDS [6, 9]

p-Nitrobenzyl bromide will give mono-, di- or tri-substituted derivatives with substituted barbituric acids according to the number of substituents already in the molecule. Thus the *p*-nitrobenzyl radical will replace the hydrogens attached either to the carbon or to the nitrogen. The reaction with veronal can be represented.



$$\begin{array}{rcl} & CO & \!-\!NH \\ & | & \ \ | \\ (C_2H_5)_2 & C & \ \ CO \\ & | & \ \ | \\ & CO & \!-\!NH \end{array} + 2NO_2C_6H_4\cdot CH_2Br \longrightarrow \begin{array}{lcl} CO & \text{———} & N\cdot CH_2\cdot C_6H_4\cdot NO_2 \\ | & & | \\ C(C_2H_5)_2 & & CO \\ | & & | \\ CO & \text{———} & N\cdot CH_2\cdot C_6H_4\cdot NO_2 \end{array} + 2HBr$$

Preparation of Derivatives

For substituted barbituric acids with two replaceable hydrogens, dissolve 0·5 g. of acid and 0·25 g. anhydrous sodium carbonate in 5 ml. water. Warm to dissolve and then add 1·1 g. *p*-nitrobenzyl bromide dissolved in 10 ml. alcohol. Reflux for one hour. Should no derivative separate on cooling, add water to the hot solution until a cloudiness persists and then cool and filter. Wash well with water, then with a small quantity of alcohol and finally with ether.

Recrystallise the product from water or alcohol, or dissolve in chloroform and reprecipitate with alcohol.

For melting points of derivatives, *see* page 140.

PHENOLS [2, 5]

p-Nitrobenzyl bromide reacts with phenols to give ethers of definite melting points suitable for the characterisation of the phenols.

$$R\cdot OH + NO_2\cdot C_6H_4\cdot CH_2Br \longrightarrow NO_2C_6\cdot H_4\cdot CH_2OR + HBr$$

Preparation of Derivatives

Dissolve 1 g. of the phenol and 1 g. of reagent in 25 ml. alcohol and 1 ml. 5N sodium hydroxide and reflux for one hour. Add 5 to

10 ml. water to dissolve any alkali bromide and then make the solution alkaline to litmus. Cool, filter off the *p*-nitrobenzyl ether and recrystallise from alcohol or from aqueous alcohol.

For melting points of derivatives, *see* page 155.

OTHER APPLICATIONS

p-Nitrobenzyl bromide has been proposed as a reagent for the identification of a limited number of primary and secondary aromatic amines [8], but in view of the number of satisfactory reagents which are available, this application has not been deemed worthy of fuller treatment.

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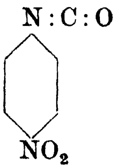
p-NITROPHENYL *iso*-CYANATE

(*p*-Nitrophenyl Carbimide)



Mol. Wt. 164·1

Reagent for Alcohols and Primary and Secondary Amines

p-Nitrophenyl *iso*-cyanate is a yellow crystalline substance of melting point 56–57°. It is soluble in carbon tetrachloride, benzene and other non-hydroxylic solvents. The solid reacts very readily with atmospheric moisture, yielding the much less soluble di-*p*-nitrophenyl urea and on this account must be stored in well-closed containers. It has none of the lachrymatory properties of phenyl *iso*-cyanate.

ALCOHOLS

With alcohols *p*-nitrophenyl *iso*-cyanate forms urethanes which have higher melting points than those derived from phenyl *iso*-cyanate.

$$NO_2 \cdot C_6H_4N : C : O + R \cdot OH \longrightarrow NO_2 \cdot C_6H_4 \cdot NH \cdot COOR$$

Preparation of Derivatives

For the lower alcohols Shriner [1, 5] recommends mixing the *iso*-cyanate with an excess of the alcohol in benzene solution; a spontaneous reaction occurs, the benzene is evaporated off and the urethane recrystallised from carbon tetrachloride. We have found it quite as satisfactory to carry out the reaction in carbon tetrachloride, filter the hot solution and allow to crystallise. Methyl- and ethyl-*p*-nitrophenyl-urethanes are not very soluble in carbon tetrachloride but can be crystallised quite satisfactorily if sufficient solvent is used. The higher alcohols, from octyl upwards, are treated with the *iso*-cyanate in petroleum ether and the urethanes recrystallised from 50 per cent. alcohol [3, 4].

For melting points of derivatives, *see* page 115.

AMINES

p-Nitrophenyl *iso*-cyanate yields substituted ureas with primary and secondary amines.

$$NO_2 \cdot C_6H_4 \cdot N : C : O + NH_2 \cdot R \longrightarrow NO_2 \cdot C_6H_4 \cdot NH \cdot CONH \cdot R$$

The derivatives obtained from aliphatic amines give good differentiation on melting points in certain cases but the melting points for aromatic derivatives [7] are inconveniently high and are, in many cases, accompanied by decomposition. For this reason only the aliphatic series are included in the tables.

Preparation of Derivatives

The general procedure is to mix benzene solutions of *iso*-cyanate and amine and to precipitate the substituted urea with petroleum ether. The derivative is then recrystallised from ethyl alcohol.

For melting points of derivatives of
(*a*) primary amines, *see* page 127.
(*b*) secondary amines, *see* page 136.

OTHER APPLICATIONS

The reagent has also been investigated with respect to amino-acids and substituted hydrazines. With the former it yields derivatives of hydantoic acid or hydantoin and with the latter substituted semicarbazides. For particulars of these methods and derivatives reference should be made to Hoogstraten's paper [3].

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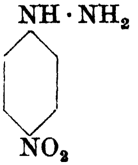
p-NITROPHENYLHYDRAZINE



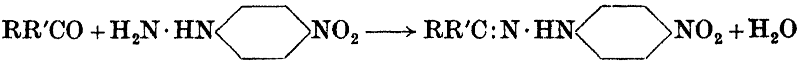
Mol. Wt. 153·1

Reagent for Aldehydes and Ketones

The reagent, an orange crystalline solid of M.P. 157°, is probably the best of its type, condensing with aldehydes and ketones to yield crystalline derivatives with convenient melting points. The reagent itself slowly decomposes if exposed for long at room temperature but may safely be stored in a refrigerator indefinitely. It is insoluble in water but easily soluble in hot alcohol.

Preparation of Derivatives

Equivalent amounts of the carbonyl compound and *p*-nitrophenylhydrazine conforming to the equation



are dissolved in glacial acetic acid and refluxed for 15 to 30 minutes. The derivative usually crystallises out on cooling, or, if not, will do so on careful dilution with water. The solid is collected and recrystallised to constant melting point (one crystallisation is normally sufficient) from a suitable solvent, usually alcohol, acetic acid or nitrobenzene.

For melting points of derivatives of
(*a*) aldehydes, *see* page 120. (*b*) ketones, *see* page 146.

Properties of *p*-Nitrophenylhydrazones

p-Nitrophenylhydrazones give good Janovsky reactions, intense red or violet colours being given when the solution in acetone is treated with 5N sodium hydroxide.

By contrast neither *o*- nor *m*-nitrophenylhydrazones give any red colour. The result of a test should, however, be interpreted with caution since, for example, *p*-nitrobenzaldehyde *o*-nitrophenylhydrazone gives an intense green colour under these conditions.

OTHER APPLICATIONS

The sparing solubility of furfural and methyl-furfural *p*-nitrophenylhydrazones are such that the reagent has been used for the estimation of these aldehydes [18]. The reagent has also found use in the determination of acetone [17], in the detection of formaldehyde [9] and as a microchemical reagent for aldehydes and ketones [5].

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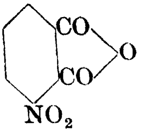
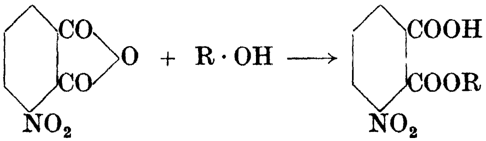
3-NITROPHTHALIC ANHYDRIDE



Mol. Wt. 193·1

Reagent for Alcohols

3-Nitrophthalic anhydride is a yellow crystalline solid melting at 163–164°. It readily reacts with aliphatic alcohols with the formation of mono-esters in accordance with the equation :



a small quantity of the isomeric ester is formed at the same time but this is completely removed on recrystallisation. The melting points of the esters are rather close together but the derivatives have a free carboxyl group so that the equivalent weights can easily be determined by titration with standard alkali.

Preparation of Derivatives [1]

A quantity of anhydride is treated with half its weight of alcohol and heated on a water-bath for 10 minutes. The product is dissolved in hot water, crystallised, filtered off and dried.

In the case of aqueous alcoholic solutions it is advisable to add potassium carbonate in excess and to pipette off the alcohol layer for testing purposes.

For melting points of derivatives, *see* page 115.

OTHER APPLICATIONS

The reagent has also been employed, but is not recommended for the identification of mercaptans [2].

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PHENACYL BROMIDE

(ω-Bromoacetophenone)

$C_6H_5 \cdot CO \cdot CH_2Br$

Mol. Wt. 199·1

Reagent for Carboxylic Acids

Phenacyl bromide is a white crystalline solid which melts at 48–50° and which discolours on keeping. The substance is insoluble in water but soluble in alcohol. The reagent is particularly useful for the identification of organic acids, for the latter are converted to crystalline phenacyl esters.

$$C_6H_5 \cdot CO \cdot CH_2Br + R \cdot COOH \longrightarrow R \cdot COO \cdot CH_2 \cdot CO \cdot C_6H_5 + HBr$$

Preparation of Derivatives

Dissolve 1 g. phenacyl bromide in 10 ml. alcohol and add the sodium salt of the acid dissolved in 5 ml. water. Reflux for a period depending upon the basicity of the acid, one hour for a monobasic acid, two hours for a dibasic acid and three hours for tribasic. When identifying polybasic acids it is advisable to use an excess of the reagent. Cool the solution, filter off the phenacyl ester and wash with two 5 ml. portions of aqueous alcohol and then twice with 5 ml. portions of water. Recrystallise the product from alcohol or from aqueous alcohol..

For melting points of derivatives, *see* page 110.

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PHENYL *iso*-CYANATE

(Phenyl Carbimide)

$C_6H_5 \cdot N : C : O$

Mol. Wt. 119·1

Reagent for Alcohols, Phenols and Alkyl Halides

Phenyl *iso*-cyanate is a colourless liquid boiling at 160–163°. Its vapour, even at normal temperatures, is irritant and lachrymatory. The liquid reacts very readily with water and must be protected from atmospheric moisture by well-closed containers. In spite of such protection it may come to contain some crystals of carbanilide, the product of reaction with water, but traces of this impurity are separated in the ordinary course of preparing derivatives.

ALCOHOLS AND PHENOLS

The reagent forms urethanes or carbanilates by reaction with alcohols and phenols.

$$C_6H_5 \cdot N : C : O + R \cdot OH \longrightarrow C_6H_5 \cdot NH \cdot COOR$$

The derivatives so obtained are readily crystallised and show well-defined melting points, though in the case of the alcohols the melting points are rather low.

Preparation of Derivatives

The alcohol or phenol should be practically free from water, since water reacts preferentially with the *iso*-cyanate yielding carbanilide. A sample is mixed in a dry test-tube with a little less than one equivalent of the reagent. With many of the alcohols the reaction is spontaneous and the mixture becomes warm, but in all cases the reaction should be completed by heating for a few minutes in a boiling water-bath. On cooling, the derivative solidifies and is recrystallised from petroleum ether or carbon tetrachloride. We have found petroleum ether, B. Pt. 80–100° or 100–120°, to yield very satisfactory crystallisations, any carbanilide which is present being quite insoluble and easily removed by filtration.

Secondary alcohols react less readily than primary and the tertiary alcohols still less readily [9]. Polyhydric alcohols react generally with each hydroxyl group when heated to 150–200° with the *iso*-cyanate. These derivatives are best crystallised from alcohol after washing out any unreacted *iso*-cyanate with ether or benzene, but it is often difficult to induce them to show satisfactory melting points [2]. Polyhydric phenols are heated 10–15 hours in a sealed tube at 100° [1].

Negative groups hinder the reaction of phenols with phenyl *iso*-cyanate but the derivatives of the mono-nitrophenols have been obtained by boiling with the reagent in toluene for 3 hours, when the urethanes will crystallise on cooling [5]. We have found it more convenient and successful to employ the catalytic effect of tertiary amines discovered by French and Wirtel in their work on α-naphthyl *iso*-cyanate. For example, the addition of 2–3 drops of an ethereal solution of trimethylamine to a mixture of *o*-nitrophenol and phenyl *iso*-cyanate brings about an immediate reaction. We were unsuccessful in preparing this derivative by other means.

For melting points of derivatives of

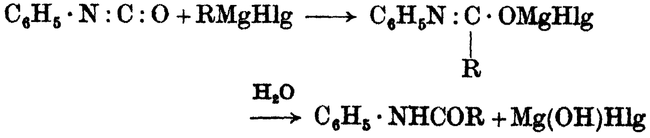
(*a*) alcohols, *see* page 115.

(*b*) phenols, *see* page 155.

A further series of melting points for derivatives of uncommon phenols is also to be found from bibliography reference [13].

ALKYL HALIDES

Phenyl *iso*-cyanate reacts according to the following scheme with the Grignard reagents prepared from the alkyl halides.



$$C_6H_5\cdot N:C:O + RMgHlg \longrightarrow C_6H_5N:\underset{\overset{|}{R}}{C}\cdot OMgHlg$$

$$\xrightarrow{H_2O} C_6H_5\cdot NHCOR + Mg(OH)Hlg$$

The product of the reaction is, therefore, the anilide of the acid containing one more carbon atom than the alcohol radical.

Preparation of Derivatives

The following procedure is quoted from the paper cited under [15]:

'In a dry test-tube with a cork bearing a calcium chloride tube is placed 0·4 g. (17 milliatoms) of magnesium turnings. A small crystal of iodine is added and the tube is heated gently until the iodine has reacted completely. The tube is allowed to cool and a solution of 1–2 g. (approximately 10 millimoles) of the dry alkyl halide in 4–5 ml. of dry ether is added. With many halides the reaction starts vigorously, and it is necessary to cool the tube in a bath of cold water. In these cases it is preferable to add slowly the solution of the alkyl halide to the magnesium. If the reaction does not start spontaneously the tube is heated gently by immersion in a beaker of warm water. After the reaction has started the ether is maintained in gentle ebullition until the alkyl halide has reacted completely. After cooling, about 10 ml. of dry ether is added and the un-reacted magnesium is allowed to settle. The solution is decanted quickly into another dry test-tube of large capacity, and 4–5 ml. of a 10 per cent. ethereal solution of phenyl *iso*-cyanate (3–4 millimoles) is added dropwise, with shaking. The tube is protected from atmospheric moisture and allowed to stand for a few minutes with intermittent shaking. The reaction mixture is poured cautiously into 20 ml. of ice water containing 1 ml. of concentrated hydrochloric acid and the mixture is agitated thoroughly. The ether layer is separated, dried over anhydrous magnesium sulphate and evaporated. The residual crude anilide is crystallised from appropriate solvents and if necessary decolorised by the addition of a little decolorising carbon.'

For melting points of derivatives, *see* page 142.

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PHENYLHYDRAZINE HYDROCHLORIDE

$C_6H_5 \cdot NH \cdot NH_2 \cdot HCl$

Mol. Wt. 144·6

Reagent for Aldehydes and Ketones

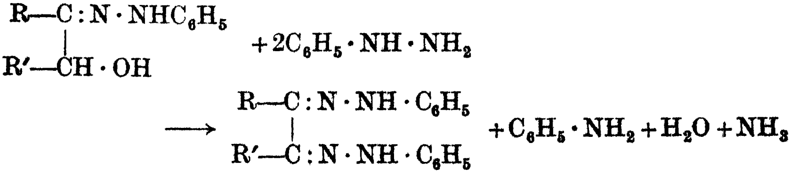
Phenylhydrazine hydrochloride is a white or pale cream-coloured crystalline powder which is liable to become brown and unfit for use if exposed unduly to air and light. It is soluble in water and in alcohol.

With carbonyl compounds phenylhydrazine reacts to form phenylhydrazones.

$$RR'C:O + H_2N \cdot NH \cdot C_6H_5 \rightarrow RR'C:N \cdot NHC_6H_5 + H_2O$$

The derivatives yielded by the lower aldehydes and ketones are often oils or low-melting solids difficult to crystallise, and although the reagent is quite useful in some instances it has become largely superseded by the nitro-substituted phenylhydrazines.

α-Hydroxyaldehydes and ketones with an excess of phenylhydrazine yield osazones by oxidation of the α-hydroxyl group and condensation with a second molecule of phenylhydrazine.



$$\begin{array}{l} R\text{—}C:N \cdot NHC_6H_5 \\ \quad | \\ R'\text{—}CH \cdot OH \end{array} + 2C_6H_5 \cdot NH \cdot NH_2 \longrightarrow \begin{array}{l} R\text{—}C:N \cdot NH \cdot C_6H_5 \\ \quad | \\ R'\text{—}C:N \cdot NH \cdot C_6H_5 \end{array} + C_6H_5 \cdot NH_2 + H_2O + NH_3$$

The formation of osazones is of importance in the study of the sugars [3] but this subject is not within the scope of the present volume.

α-Diketones react normally yielding mono- and di-hydrazones or osazones while β-diketones yield pyrazoles.

Phenylhydrazine has also been applied to the characterisation of eight aliphatic sulphonic acids, methyl to *n*-octyl, but in view of the rarity of these acids the reader is referred for details to the literature [5].

Preparation of Derivatives

A solution of phenylhydrazine is prepared by dissolving 1 g. of the hydrochloride and 1·5 g. of sodium acetate in 10 ml. of water. The aldehyde or ketone is dissolved in a little alcohol and added to an excess of the phenylhydrazine solution and the mixture warmed on a steam bath for about 30 minutes, more alcohol being added if necessary to dissolve the aldehyde or ketone. The phenylhydrazones often separate first as oils on cooling. Purification is effected by recrystallisation usually from alcohol, though dilute alcohol, water, benzene or ligroin may sometimes be found more suitable. The alcohol employed in the preparation or purification of phenylhydrazones must be free from aldehydes and ketones.

A 30 to 50 per cent. acetic acid solution of the liquid phenylhydrazine base is also commonly employed for the preparation of phenylhydrazones but the hydrochloride is more stable and more convenient to handle.

Some substances apparently require a considerable departure from the standard procedure outlined above, and in some cases variations in the method of preparation lead to alternative derivatives. Where circumstances are thus complicated the use of some other reagent is generally to be preferred.

The phenylhydrazones tend to undergo transformation to derivatives of indole with loss of ammonia and, for this reason, it is advisable to determine their melting points without delay.

For melting points of derivatives of

(*a*) aldehydes, *see* page 120.

(*b*) ketones, *see* page 146.

Quantitative Methods

Quantitative methods for some aldehydes and ketones have been devised [4].

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4-PHENYLSEMICARBAZIDE

$C_6H_5 \cdot NH \cdot CO \cdot NH \cdot NH_2$

Mol. Wt. 123·2

Reagent for Aldehydes and Ketones

4-Phenylsemicarbazide occurs as a white crystalline substance, of melting point 120–123°. With aldehydes and ketones it undergoes condensation, yielding phenylsemicarbazones.

$$RR' \cdot C : O + H_2N \cdot NH \cdot CO \cdot NH \cdot C_6H_5 \longrightarrow RR'C : N \cdot NH \cdot CO \cdot NH \cdot C_6H_5 + H_2O$$

These derivatives crystallise well and have sharply defined melting points.

Preparation of Derivatives

A solution of 0·5 g. of 4-phenylsemicarbazide in 5 ml. alcohol is acidified with a few drops of acetic acid and to it is added a solution of a molecular equivalent of the aldehyde or ketone in 5 ml. of alcohol. The mixture is heated for a few minutes in a water-bath and filtered hot. On cooling, the phenylsemicarbazone crystallises, though dilution with water may sometimes be necessary. It is recrystallised from alcohol or diluted alcohol.

For melting points of derivatives of

(*a*) aldehydes, *see* page 120.

(*b*) ketones, *see* page 146.

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PHENYL *iso*-THIOCYANATE

$C_6H_5 \cdot N : C : S$

Mol. Wt. 135·2

Reagent for Primary Amines and Nitriles

Phenyl *iso*-thiocyanate is a pale yellow liquid boiling at 117–118° at a pressure of 34–35 mm. It is insoluble in water but soluble in alcohol and does not react readily with either; the latter may, in consequence, be employed as a solvent in the preparation of derivatives.

AMINES

The reagent yields substituted thioureas with amines both aliphatic and aromatic.

$$C_6H_5NCS + R \cdot NH_2 \longrightarrow C_6H_5NH \cdot CS \cdot NHR$$

In the aliphatic series the derivatives are difficult to crystallise and of rather low melting points. Although the reagent reacts with secondary amines its use appears to have been limited to the characterisation of the primary class. Certain substitution products of aniline fail to give thioureas with the reagent. This applies, though not invariably, to di-ortho substituted compounds, while NO_2 substituted in the 2 or 4 position prevented condensation in all the cases investigated by Goehring and Pottebaum [2]. These authors prepared derivatives from a series of halogen and nitro-substituted anilines which, on account of their rarity, are not included in our tables.

Preparation of Derivatives

The calculated quantity of the reagent is added to a solution of the amine in alcohol when, in many cases, a spontaneous reaction occurs and the thiourea crystallises when the solution cools. If the reaction takes place less readily, as is common with aromatic amines, the solution is heated to boiling or the reactants are heated together without solvent over a low flame. The derivative is recrystallised from alcohol or dilute alcohol.

For melting points of amine derivatives, *see* pages 127 and 129.

NITRILES [3]

The reagent has been applied to the characterisation of a limited number of nitriles after reduction of the latter to amines.

$$R \cdot CN + 4H \longrightarrow R \cdot CH_2 \cdot NH_2$$

In the aromatic series the yields are poor, and the aliphatic nitriles yield eventually the same rather unsatisfactory derivatives as the amines. It would appear that the procedure would find more useful application to the aliphatic nitriles if α-naphthyl *iso*-thiocyanate were employed in place of phenyl *iso*-thiocyanate. The experimental details are as follows :

Preparation of Derivatives

One gram of the nitrile is dissolved in 20 ml. of absolute alcohol in a flask fitted with a reflux condenser. Reduction is achieved by adding 1·5 g. of sodium in small pieces through the condenser at such a rate as to maintain a vigorous reaction, the flask being held in a water-bath at 50–60°. The solution is then cooled and acidified by the cautious addition of 10 ml. of hydrochloric acid (s. g. 1·18) through the condenser. The mixture is distilled until 20 ml. of distillate are collected, again cooled, and made alkaline by the cautious addition of a strong solution of sodium hydroxide (6 g. in 6 ml. water). The contents of the flask are again distilled with the end of the condenser dipping into about 3 ml. of water and the heating continued until the residue of sodium chloride is almost dry. The distillate is shaken vigorously with 1 ml. of phenyl *iso*-thiocyanate until the solid derivative separates, and this is purified in the usual manner.

For melting points of derivatives, refer to the tables of primary aliphatic amines, page 127, and primary aromatic amines, page 129.

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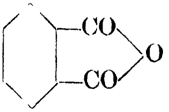
PHTHALIC ANHYDRIDE



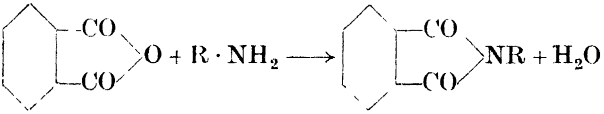
Mol. Wt. 148·1

Reagent for Primary Amines and Aromatic Hydrocarbons

Phthalic anhydride is supplied in the form of white flakes. It melts at 129–131°, is slightly soluble in cold water, more soluble in hot water forming phthalic acid, and is soluble in alcohol and in ether.

AMINES [2]

Phthalic anhydride has been employed as a reagent for amines and under the conditions described below reacts only with primary amines. Thus the reagent can be used to separate primary from secondary and tertiary amines.



Preparation of Derivatives

Dissolve 1 g. of the amine and 1 g. phthalic anhydride in 10 ml. glacial acetic acid and reflux for about 30 minutes. On cooling, the N-substituted phthalimide crystallises out. Recrystallise from an appropriate solvent, usually alcohol, glacial acetic acid, or *o*-dichlorobenzene.

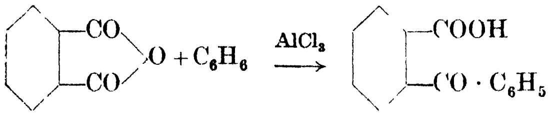
With certain ortho-substituted amines it is advisable to add two drops of sulphuric acid to catalyse the reaction. With amine salts, particularly the aliphatic amine salts, it is stated that the reaction with phthalic anhydride does not proceed easily, and in such cases it is suggested that the condensation be carried out in the presence of anhydrous sodium acetate.

For melting points of derivatives of

(*a*) primary aliphatic amines, *see* page 127.
(*b*) primary aromatic amines, *see* page 129.

AROMATIC HYDROCARBONS [1]

o-Aroylbenzoic acids, prepared by condensing phthalic anhydride with aromatic hydrocarbons in the presence of aluminium chloride, serve as useful derivatives for certain hydrocarbons. These derivatives have definite melting points and can be titrated with alkali. In this way phthalic anhydride is a good reagent for benzene and toluene but it will not differentiate between the isomeric xylenes. It should be noted that the benzene and toluene derivatives crystallise as hydrates and readily lose their water of crystallisation at 100° ; the melting points quoted in the table are for the anhydrous compounds.



Preparation of Derivatives

To an intimate mixture of 0·4 g. phthalic anhydride and 0·8 g. anhydrous aluminium chloride add 10 ml. carbon disulphide and 0·4 g. of the hydrocarbon. Heat on a water-bath under reflux until no more hydrochloric fumes are evolved. Cool under the tap, and if two layers form, separate off the upper carbon disulphide layer. Add 10 ml. 6N hydrochloric acid drop by drop with shaking. Filter off and wash the solid with cold water. Boil the crude *o*-aroylbenzoic acid with 10 ml. 6N ammonia, 20 ml. water and a little charcoal. Filter, cool and acidify with dilute hydrochloric acid. Filter off the solid, wash and recrystallise from aqueous alcohol.

As noted above, the benzene and toluene derivatives are the only two which crystallise as hydrates and these should be transferred to a watch-glass and dried at 100°.

For melting points of derivatives, *see* page 144.

OTHER APPLICATIONS

With aliphatic alcohols, phthalic anhydride readily forms alkyl hydrogen phthalates [3], but as a number of these compounds are not easy to isolate, 3-nitrophthalic anhydride is to be preferred for the characterisation of alcohols.

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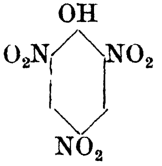
PICRIC ACID

(2 : 4 : 6 -Trinitrophenol)



Mol. Wt. 229·1

Reagent for Aromatic Hydrocarbons, Amines, Phenols, Alkaloids, Heterocyclic Compounds and Aromatic Ethers

Picric acid is a bright yellow crystalline substance melting at 122°, soluble in water (1 in 70 cold, 1 in 15 hot) and in cold alcohol (1 in 20). It forms addition compounds with the above-named classes of organic substances and these derivatives are recommended for their speed of preparation and for the simplicity of technique required.

Preparation of Derivatives

The derivatives are prepared by mixing hot solutions of the two components in a single solvent, usually alcohol, acetic acid, acetone or water, and cooling, when the derivative separates in crystalline condition. Benzene, ether or chloroform is sometimes employed when the picrate is unstable to water or hydroxylic solvents, e.g. anthracene or fluorene picrate. The lower aromatic hydrocarbons (benzene, toluene, etc.) yield picrates when the reagent is refluxed with the hydrocarbon until dissolved and the solution allowed to cool. On attempting to determine the melting point, however, the hydrocarbon gradually evaporates off, leaving pure picric acid of melting point 122°.

The large majority of derivatives have the general formula 1 mol. substance : 1 mol. picric acid and should be recrystallised from the original solvent until of constant melting point. This is normally accomplished in one recrystallisation.

Titration of Derivatives

The derivatives may be further commended since they may be titrated against standard sodium hydroxide using ethyl bis-2 : 4-dinitrophenyl acetate as indicator. This indicator, employed as a 1 per cent. solution in equal volumes of acetone and alcohol, gives a colour change from colourless to blue in the titration of a weak acid with a strong base, and is therefore very well suited to the titration of yellow picrate solutions. The titre directly indicates the picric acid content of the derivative and indirectly the molecular weight of the unknown component, assuming an equimolecular composition. Other methods of estimating the picric acid content are to titrate with methylene blue solution [22], or titanous chloride [7, 8], or to decompose with sodium hydroxide and measure the sodium picrate by a photometric method [23].

From the viewpoint of recovery of material, purification via the picrate may be recommended. The picrate, after purification, is treated with warm dilute sodium hydroxide or ammonia and the original compound (if insoluble in alkali) separated by usual means.

In conclusion, mention should be made of the method used to identify some compounds which behave abnormally, e.g. 3 : 4-xylen-ol. In this particular case the xylenol is fused with an equivalent weight of reagent (1·9 g. per gram of xylenol) and the yellow compound obtained recrystallised from alcohol (Huntress and Mulliken).

For melting points of derivatives, of

(*a*) aromatic hydrocarbons, *see* page 144.

(*b*) primary aliphatic amines, *see* page 127.

(*c*) primary aromatic amines, *see* page 129.
(*d*) secondary amines, *see* page 136.
(*e*) tertiary amines, *see* page 138.
(*f*) phenols, *see* page 155.
(*g*) alkaloids, *see* page 124.
(*h*) heterocyclic compounds, *see* page 143.
(*j*) aromatic ethers, *see* page 141.

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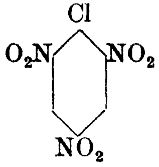
PICRYL CHLORIDE

(2 : 4 : 6-Trinitrochlorobenzene)



Mol. Wt. 247·5

Reagent for Primary and Secondary Amines

Picryl chloride is a yellow crystalline solid melting at about 83°, soluble in 45 parts cold or 4 parts boiling alcohol. The cold 2 per cent. alcoholic solution used for analysis remains stable for at least one month.

The reagent condenses with primary and secondary amines in alcoholic solution to form derivatives as follows :

$$(NO_2)_3 \cdot C_6H_2 \cdot Cl + R \cdot NH \cdot R' \longrightarrow (NO_2)_3 \cdot C_6H_2 \cdot NRR' + HCl$$

The resulting picramides are stable, sparingly soluble in cold alcohol and melt sharply with little decomposition. They crystallise well and have brilliant colours. The colours of the derivatives produced from isomeric amines are frequently strikingly different, e.g. *o*-anisidine gives a violet coloured derivative, *p*-anisidine a bright red compound. In almost all cases the yield of derivative obtained is excellent.

Owing to the slower rate of condensation, it is not as useful for secondary amines although excellent results are obtained in some cases, e.g. piperidine and diethanolamine.

The diamino compounds and nitroamines are better characterised with other reagents, e.g. formic acid.

Preparation of Derivatives

Dissolve 0·25 g. of a solid amine in 2 ml. hot alcohol and add 20 ml. of a 2 per cent. alcoholic reagent solution. Heat to boiling, cool, scratch (or add water) and filter off. Wash with a little cold alcohol and recrystallise from alcohol, glacial acetic acid or a mixture of the two. Collect, wash with a little alcohol and dry in warm air.

Liquid amines should be added to the reagent solution until present in slight excess (when a red colour is given that does not change on shaking).

Amphoteric amino compounds and also those containing nitro groups are best treated as follows :

Separately dissolve equimolecular amounts of the amine and the reagent in 50 per cent. alcohol, mix the hot solutions and add a solution of one to two molecular proportions of sodium hydroxide in the same solvent. On cooling, the required derivative crystallises out. This modification of the general method gives very good results with the aminobenzoic acids.

For melting points of derivatives of

(*a*) primary aliphatic amines, *see* page 127.
(*b*) primary aromatic amines, *see* page 129.
(*c*) secondary amines, *see* page 136.

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SEMICARBAZIDE HYDROCHLORIDE

$NH_2 \cdot CO \cdot NH \cdot NH_2 \cdot HCl$

Mol. Wt. 111·5

Reagent for Aldehydes and Ketones

Semicarbazide hydrochloride is a white crystalline compound melting at 173–175°. It is readily soluble in water but practically insoluble in alcohol.

The base condenses with aldehydes and with ketones yielding semicarbazones :

$$RR'C:O + H_2N \cdot NH \cdot CO \cdot NH_2 \longrightarrow RR'C:N \cdot NH \cdot CO \cdot NH_2 + H_2O$$

Preparation of Derivatives

The reaction is usually brought about by adding the aldehyde or ketone to a strong aqueous solution of semicarbazide hydrochloride in which the mineral acid has been neutralised by the addition of an equivalent quantity of sodium acetate, adding alcohol, if necessary, to produce a clear solution. A small excess of semicarbazide is generally employed. The semicarbazone commonly crystallises in the course of a few minutes, though some require a much longer period, and may be recrystallised from water, alcohol or acetone. Hopper [5] devised a method in which the sodium acetate is conveniently replaced by pyridine. For example, 5 g. of acetophenone is dissolved in 20 ml. of pyridine and the solution added to a solution of 5 g. of semicarbazide hydrochloride dissolved in 8 ml. of water. The semicarbazone crystallises readily from the aqueous pyridine.

For melting points of derivatives of

(*a*) aldehydes, *see* page 120.
(*b*) ketones, *see* page 146.

Quantitative Methods

The semicarbazones, in common with other derivatives of hydrazine, may conveniently be titrated with standard iodate solution [13]. The weighed sample is dissolved in 50 ml. of 5N hydrochloric acid to bring about hydrolysis and to provide conditions for stability of the iodine chloride which is present at the end-point. In certain cases it is necessary to heat the acid solution to 100° in order to complete the hydrolysis. The solution is titrated with M/20 potassium iodate solution until the deep brown colour first formed becomes light, then a few ml. of chloroform are added and the titration continued with vigorous shaking until the chloroform is colourless.

$$NH_2 \cdot CO \cdot NH \cdot NH_2 + KIO_3 + 2HCl \longrightarrow NH_3 + CO_2 + N_2 + ICl + KCl$$

This method of determination is not general in its application since certain carbonyl compounds, e.g. furfural, interfere with the titration.

Other quantitative methods have also been recommended [6, 10, 11, 12].

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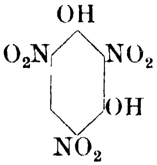
STYPHNIC ACID

(2 : 4 : 6-Trinitro-resorcinol)



Mol. Wt. 245·1

Reagent for Hydrocarbons and Alkaloids

Styphnic acid, a yellow crystalline solid melting at about 176°, is capable of yielding addition compounds with both the above-named classes of compounds in much the same manner as picric acid. The compounds formed do not crystallise quite as readily as the picrates and are usually obtained in smaller yield. Nevertheless they are useful derivatives, especially since reliable reagents for hydrocarbons and alkaloids are few in number.

The reagent will also form addition compounds with amines and heterocyclic bases such as carbazole and quinoline, but in view of the large number of amine reagents described, description of its use in this connection is omitted. Reference to the bibliography [1, 3] will, however, provide the necessary information.

All derivatives except those otherwise indicated in the melting point table are equimolecular. No stable derivatives are formed by benzene and its simple homologues.

Preparation of Derivatives of Aromatic Hydrocarbons

A mixture of 1·25 g. reagent and 1/200 mol of the hydrocarbon is dissolved in 5–10 ml. acetic acid by heat and the solution allowed to cool and crystallise. The derivative is filtered off, washed with acetic acid and finally with alcohol before drying in air. After a melting point determination the derivative is recrystallised from acetic acid and the melting point redetermined. With anthracene, benzene must be employed as solvent as with other solvents dissociation occurs.

The colour of derivative obtained varies appreciably, thus :

acenaphthene	orange
fluorene	golden-yellow
naphthalene	bright yellow
phenanthrene	golden-brown
anthracene	scarlet

For melting points of derivatives, *see* page 144.

Preparation of Derivatives of Alkaloids

A mixture of 1·25 g. reagent and 1/200 or 1/400 mol of the alkaloid (depending on the basicity of the latter) is dissolved in boiling alcohol or acetic acid and allowed to crystallise. After collection the derivative is recrystallised from alcohol (95 per cent. or less), acetic acid or methyl ethyl ketone (quinine derivative).

For melting points of derivatives, *see* page 124.

Titration of Derivatives

It is stated [4, 5, 6] that styphnates may be accurately titrated against decinormal sodium hydroxide using phenolphthalein as indicator. Trial has shown, however, that when this indicator is used, an end-point (very indefinite) is given before *both* hydroxyl groups have been neutralised. At best, therefore, titration can only give a very approximate indication of the molecular weight of the alkaloid or hydrocarbon. The use of thymolphthalein gives no improvement in end-point.

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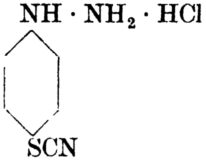
p-THIOCYANOPHENYLHYDRAZINE HYDROCHLORIDE



Mol. Wt. 201·5

Reagent for Aldehydes and Ketones

p-Thiocyanophenylhydrazine hydrochloride, a recent addition to the phenylhydrazine class of reagents for the carbonyl group, is a white or greyish white solid melting at 188° with decomposition. By virtue of the large number of derivatives described by Horii and the fact that the derivatives are well crystallised and of not too high melting point, this reagent deserves mention.

Preparation of Derivatives

A mixture of *p*-thiocyanophenylhydrazine hydrochloride and an equivalent weight of crystalline sodium acetate (0·7 g. per gram) as determined by the equation

$$NCS \cdot C_6H_4 \cdot NH \cdot NH_2 \cdot HCl + NaAc = NCS \cdot C_6H_4 \cdot NH \cdot NH_2 \cdot HAc + NaCl$$

is dissolved in a mixture of absolute alcohol and water. To the solution is added a solution of the carbonyl compound in absolute alcohol and the whole refluxed for 5 to 10 minutes.

The derivative either crystallises on cooling, or will do so on careful dilution with water and scratching. After filtration the derivative is recrystallised from a suitable solvent such as 70 per cent. alcohol and dried in air.

For melting points of derivatives of

(*a*) aldehydes, *see* page 120.
(*b*) ketones, *see* page 146.

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THIOSEMICARBAZIDE

$NH_2 \cdot NH \cdot CS \cdot NH_2$

Mol. Wt. 91·1

Reagent for Aldehydes and Ketones

Thiosemicarbazide is a white crystalline substance of melting point 181–183°, soluble in about 100 parts of water at normal temperature, much more soluble in hot water, and only slightly soluble in alcohol. It forms thiosemicarbazones with aldehydes and ketones just as semicarbazones are formed from the more commonly employed semicarbazide.

$$RR'C:O + H_2N \cdot NH \cdot CS \cdot NH_2 \rightarrow RR'C:N \cdot NH \cdot CS \cdot NH_2 + H_2O$$

The thiosemicarbazones possess the distinctive property of forming insoluble compounds of the type

$$RR' \cdot C:N \cdot N:CSM \cdot NH_2 \quad (M = \text{monovalent metal})$$

with silver, copper and mercury. The precipitation of the silver compounds has been proposed [1] as an aid to the separation of carbonyl compounds from mixtures and, since the silver is readily determined, a means is thereby provided of arriving at the molecular weight of the compound. The thiosemicarbazones of the sugars do not form silver compounds.

Preparation of Derivatives

The thiosemicarbazones are prepared by heating a mixture of the aldehyde or ketone in alcohol with a strong solution of thiosemicarbazide in water. On cooling, the thiosemicarbazone crystallises from the dilute alcohol and may be crystallised from the same solvent or from water.

For the preparation of the silver compound the thiosemicarbazone must be free from any excess thiosemicarbazide since the reagent itself yields a similar compound with silver. A crude thiosemicarbazone is therefore dissolved in alcohol and any excess reagent filtered off. The filtrate is treated with silver nitrate solution and the amorphous precipitate filtered, washed and dried in a vacuum desiccator protected from light.

The silver may be determined by thiocyanate titration after decomposing the compound with hot fuming nitric acid.

The thiosemicarbazone may be recovered from the silver compound by treating an aqueous, alcoholic or ethereal suspension with hydrogen sulphide or with the theoretical quantity of hydrochloric acid. The aldehyde or ketone may be recovered by treating the thiosemicarbazone or its silver compound with mineral acid.

For melting points of derivatives of

(*a*) aldehydes, *see* page 120.

(*b*) ketones, *see* page 146.

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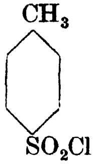
p-TOLUENESULPHONYL CHLORIDE



Mol. Wt. 190·6

Reagent for Primary and Secondary Amines and Phenols

p-Toluenesulphonyl chloride is a white crystalline powder, melting at 66–67°. It has reagent properties similar to benzenesulphonyl chloride.

AMINES

p-Toluenesulphonyl chloride can be used for the separation of primary, secondary and tertiary amines and also for the identification of primary and secondary amines. For purposes of amine separations the reader is referred to the monograph on benzenesulphonyl chloride, for *p*-toluenesulphonyl chloride is employed in precisely the same way as this reagent. The reaction between *p*-toluenesulphonyl chloride and amines may be represented as follows :

$$RNH_2 + CH_3 \cdot C_6H_4 \cdot SO_2Cl \longrightarrow CH_3 \cdot C_6H_4 \cdot SO_2NHR + HCl$$
$$RR'NH + CH_3 \cdot C_6H_4 \cdot SO_2Cl \longrightarrow CH_3 \cdot C_6H_4 \cdot SO_2NRR' + HCl$$

Preparation of Derivatives

Dissolve or suspend 2 g. of the amine in 2 ml. pyridine and add, in small amounts with shaking, 4 g. *p*-toluenesulphonyl chloride. When a primary amine is used the reaction takes place with the evolution of heat and no further heating is necessary. If no appreciable reaction occurs heat on a water-bath for 30 minutes. Cool and add water slowly ; filter off the solid and wash with dilute hydrochloric acid. Dissolve the sulphonamide, if it has been obtained from a primary amine, in hot dilute sodium hydroxide, filter and precipitate from the cold filtrate with hydrochloric acid.

Recrystallise the crude sulphonamide from alcohol.

For melting points of derivatives of
- (*a*) primary aliphatic amines, *see* page 127.
- (*b*) primary aromatic amines, *see* page 129.
- (*c*) secondary amines, *see* page 136.

PHENOLS

p-Toluenesulphonyl chloride condenses easily with phenols.

$$CH_3 \cdot C_6H_4 \cdot SO_2Cl + ROH \longrightarrow CH_3 \cdot C_6H_4 \cdot SO_3R + HCl$$

Preparation of Derivatives

Dissolve or suspend 2 g. of the phenol in 5 ml. pyridine, add 4 g. *p*-toluenesulphonyl chloride and heat on a water-bath for 15 minutes. Pour into 50 ml. cold water and stir until solid. Wash the solid with cold dilute sodium hydroxide and then with cold water. Recrystallise from ethyl or methyl alcohol.

For melting points of derivatives, *see* page 155.

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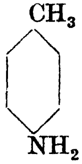
p-TOLUIDINE



Mol. Wt. 107·1

Reagent for Carboxylic Acids and Phenanthrene Monosulphonic Acids

The reagent is a white to purple solid, M.Pt., 42–45°. It is employed in precisely the same way as aniline for the identification of carboxylic acids [1], and reference should be made to the monograph on aniline for the preparation of toluidides.

For melting points of derivatives of carboxylic acids, *see* page 110.

PHENANTHRENE MONOSULPHONIC ACIDS [2]

Fieser has proposed the reagent for the identification of phenanthrene monosulphonic acids. *p*-Toluidine forms salts with the acids; the salts have definite melting points and show a large depression of melting point when impure.

Preparation of Derivatives

Treat the sodium, potassium or ferrous salt of the phenanthrene monosulphonic acid with an excess of *p*-toluidine in dilute hydrochloric acid and add sufficient water to bring into solution at the boiling point. The *p*-toluidine salt separates on cooling.

Melting Points of Derivatives

Phenanthrene-1-sulphonic acid - - -	267°
Phenanthrene-2-sulphonic acid - - -	291°
Phenanthrene-3-sulphonic acid - - -	222°
Phenanthrene-9-sulphonic acid - - -	235°

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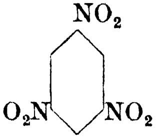
1 : 3 : 5-TRINITROBENZENE



Mol. Wt. 213·1

Reagent for Aromatic Hydrocarbons, Primary Aromatic Amines, Tertiary Amines, Heterocyclic Compounds, Phenols and Aromatic Ethers

1 : 3 : 5- or *sym*-Trinitrobenzene is a pale yellow crystalline solid melting at 121°, easily soluble in hot alcohol but insoluble in water. It furnishes addition compounds, some of which are unstable, with a wide variety of substances.

As examples of the unstable addition compounds, aniline and *o*-toluidine form derivatives when the two components are warmed together in alcoholic solution. A large excess of amine must be used as otherwise unchanged trinitrobenzene separates on cooling [4]. These bright red derivatives are unstable when (*a*) recrystallised from alcohol, (*b*) gently warmed, or (*c*) left exposed to air [1]. For this reason, when the substance has been indicated to be a homologue of aniline, the reagent should not be used for the preparation of a second derivative.

The compounds given with the naphthylamines however, are stable under all these conditions and may be recrystallised from alcohol, benzene, glacial acetic acid, acetone or chloroform.

The compounds from quinoline and *iso*-quinoline can only be prepared by fusion, as solvents dissociate them.

An interesting case of selectivity is shown by the fact that although derivatives are given by both phenols and amines, *no* such compounds are given by aminophenols.

Generally speaking, the derivatives crystallise beautifully and have brilliant colours; thus the reagent may be warmly recommended for carbazole, naphthalene, anthracene and the condensed aromatic hydrocarbons as a whole. The higher aromatic amines, whether primary, secondary or tertiary, also give excellent results with trinitrobenzene.

It should be noted that neither *m*-aminobenzoic acid nor *p*-nitroaniline give addition compounds.

Composition of Derivatives

The majority of the addition compounds are equimolecular but in several cases two molecules of the reagent combine with only one of the substance (e.g. stilbene, *o*-dianisidine and dibenzyl). In the fluorene compound, three molecules of the reagent are combined with two of fluorene. It is important to realise that phenyl-β-naphthylamine yields two compounds, in which one molecule of the amine combines with either one or two molecules of trinitrobenzene.

Preparation of Derivatives

These directions are not suitable for the preparation of addition compounds from amines containing only one benzene ring. With all other substances yielding derivatives that are stable to hot alcohol, the method of preparation is as follows :

Dissolve a mixture of equal mols of substance and reagent in hot alcohol, benzene or glacial acetic acid and allow to cool, when crystallisation occurs. Recrystallise from one of the abovementioned solvents and dry the solid in air.

For melting points of derivatives of

(*a*) hydrocarbons, *see* page 144.
(*b*) primary aromatic amines, *see* page 129.
(*c*) tertiary amines, *see* page 138.
(*d*) phenols, *see* page 155.
(*e*) heterocyclic compounds, *see* page 143.
(*f*) aromatic ethers, *see* page 141.

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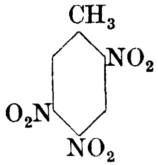
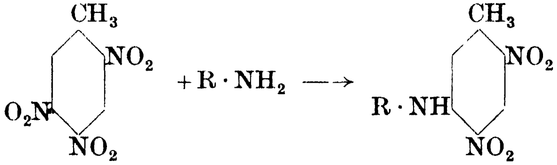
2 : 4 : 5-TRINITROTOLUENE



Mol. Wt. 227·1

Reagent for Primary Aliphatic Amines

2 : 4 : 5-Trinitrotoluene is a pale yellow highly crystalline solid of M.Pt. *ca.* 104°, readily soluble in hot alcohol and acetone. The group in position 5 is readily replaced by reaction with a *primary* amine as follows :



The dinitro-alkyl-*m*-toluidines resulting are coloured and well-crystallised solids whose melting points show a satisfactory disparity. Only a small amount of the amine is required and aqueous solutions of amines give equally good results.

Preparation of Derivatives

To a solution of 0·2 g. reagent in 5 ml. hot alcohol add 6 to 8 drops of amine or the equivalent of an aqueous solution of the amine. Separation is immediate and after boiling to redissolve the precipitate the solution is allowed to cool. After collection, the solid is recrystalised from alcohol to give yellow or orange needles.

For melting points of derivatives, *see* page 127.

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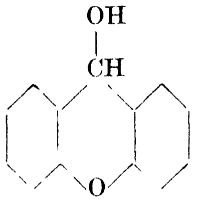
XANTHYDROL



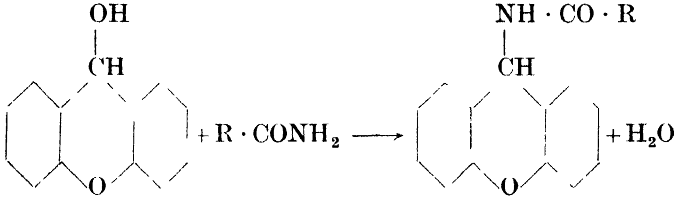
Mol. Wt. 198·1

Reagent for Amides, Urethanes, Sulphonamides and Substituted Barbituric Acids

Xanthydrol is a white crystalline solid, M.Pt. 122 124°, unstable in air and best employed for reagent purposes as a 7 per cent. *w/v* solution in glacial acetic acid. This solution is stable for several months.

AMIDES

Xanthydrol condenses with primary amides and urethanes, forming xanthyl derivatives according to the following equation,



diamides such as urea forming bis-xanthyl derivatives. Phthalimide, saccharin and succinimide also condense under these conditions. Derivatives are not, however, given by the following: dichloroacetamide, trichloroacetamide, salicylamide, oxamide, picramide, guanidine and dicyandiamide [23].

Preparation of Derivatives

Seven ml. of the reagent solution (7 per cent. *w/v*, see above) are mixed with 0·5 g. amide and refluxed for 10–15 minutes, a green solution being finally obtained. Water (5 ml.) is added and the whole allowed to cool. The resulting crystals are collected and recrystallised from aqueous dioxan. The product is washed with a little alcohol and ether and dried at 80°, as there are indications that the derivatives are hydrated.

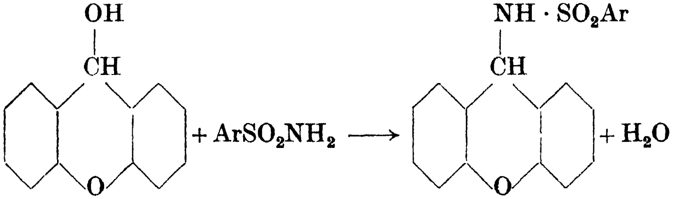
Both formamide and chloroacetamide condense slowly and require refluxing for 30 minutes before dilution.

Diamides such as urea and biuret condense immediately, the derivatives separating from the boiling solutions. Dilution in these cases is unnecessary. The derivatives thus formed are very insoluble in the usual organic solvents and have melting points dependent upon the rate of heating [5, 6]. Owing to the insolubility of the urea derivative it has found wide application in the determination of urea in urine and blood (references 1 to 20).

For melting points of derivatives, *see* page 125.

SULPHONAMIDES

Primary sulphonamides condense similarly to amides, thus



It is curious that branch-chain substituted benzene sulphonamides e.g. *p-tert*-butyl benzene sulphonamide, yield no condendensation products. No derivative is given by 2 : 4 : 6-triethyl benzene sulphonamide although the 2 : 4 : 6-trimethyl compound condenses normally. It should be noted that sulphanilamide yields a bis-derivative containing a free amino group, i.e. nuclear substitution also occurs [24].

Preparation of Derivatives

The xanthydrol solution (7 ml.) is diluted to 20 ml. with more acetic acid, 0·5 g. sulphonamide added and the whole warmed to effect complete solution. This solution is allowed to stand at room temperature for 90 minutes when the derivative will have separated.

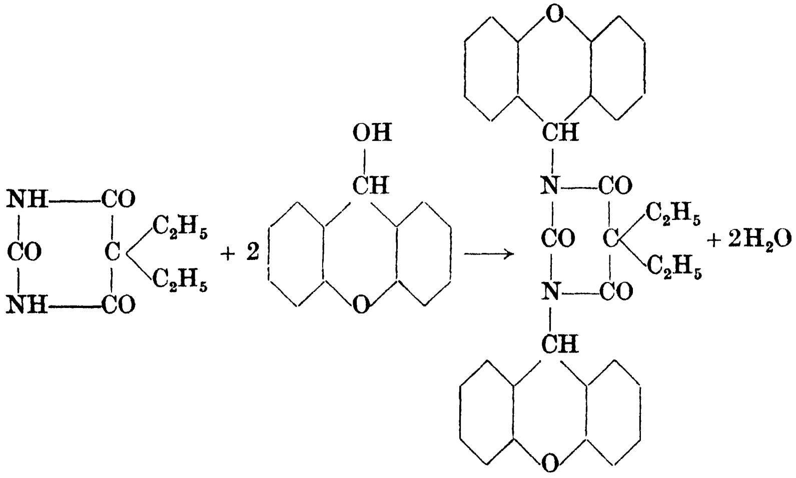
The solid is collected, recrystallised from aqueous dioxan, washed with a little alcohol and ether and dried in air.

Although the derivatives listed show comparatively little difference in melting points, mixtures of identically melting compounds show large depressions [24].

For melting points of derivatives, *see* page 161.

SUBSTITUTED BARBITURIC ACIDS

Fabre (9) has reported condensation products of xanthydrol and disubstituted barbituric acids such as veronal and has represented the reaction as follows :



Preparation of Derivatives

These derivatives are prepared by refluxing equivalent amounts of the reactants in acetic acid and allowing to cool.

Antipyrine, according to Fabre, also yields a condensation product, this being the 4–(C–) mono derivative.

For melting points of derivatives, *see* page 140.

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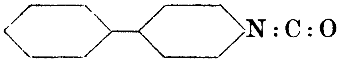
p-XENYL *iso*-CYANATE

(*p*-Xenyl Carbimide)



Mol. Wt. 195·2

Reagent for Alcohols and Phenols

p-Xenyl *iso*-cyanate is a white crystalline powder of melting point 56°, soluble in petroleum ether, carbon tetrachloride and benzene. The reagent should be stored in well-closed containers since, by reaction with atmospheric moisture, it is readily converted to di-*p*-xenyl urea. A proportion of this substance is invariably present in the material but, by virtue of its insolubility in the solvents employed, it is readily eliminated from the derivatives. By reaction with organic hydroxyl compounds free from water, urethanes or carbamates are formed, as in the case of phenyl *iso*-cyanate, but the xenyl carbamates have considerably higher melting points and on this account have been found particularly well suited to the investigation of phenolic mixtures from low temperature tar [1].

Preparation of Derivatives

The alcohol or phenol is mixed with a slight excess of *p*-xenyl *iso*-cyanate and heated for an hour at 100°. The derivative solidifies on cooling and is recrystallised from benzene or petroleum ether (B. Pt. 80–100° or 100–120°), the insoluble di-*p*-xenyl urea being filtered off.

OTHER APPLICATIONS

p-Xenyl *iso*-cyanate has also been investigated for the characterisation of amines (2) but decomposition points only are quoted for many of the derivatives. It has also been recommended as a reagent for hydrazines (3).

For melting points of derivatives of

(*a*) alcohols, *see* page 115.
(*b*) phenols, *see* page 155.

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MELTING POINT TABLES

MELTING POINT TABLES

The arrangement of the following tables is alphabetical throughout, and substances are generally named according to their derivation rather than by common names such as anthranilic acid, which is entered as *o*-aminobenzoic acid. This arrangement tends to bring chemically related substances close to one another.

Many cases occur where a *di* and sometimes a *tri* derivative may be formed. The melting point entered in all such cases except where otherwise indicated is that of the *di* or *tri* derivative. Where the *mono* derivative is the one in question this is indicated thus (m).

Other special cases arise with phenylhydrazine and substituted phenylhydrazines where the derivative obtained may be a pyrazole. In these and any other such circumstances the melting point quoted is that of the derivative which is obtained by the procedure described in the text.

The figures printed in heavy type are those which have been confirmed in the Hopkin & Williams Research Laboratories. Those in italics are from the same source and are either for melting points not previously recorded, or represent values which differ by more than 4° from those found in the literature. All such values have been obtained on derivatives recrystallised to constant melting point and prepared from substances of known purity. The identity of the derivatives has not been established by analysis, but the melting points serve the present purpose in that they refer to whatever derivative is obtained as a product of the procedure described in the text.

ACIDS, CARBOXYLIC

	Aniline	*p*-Bromophenacyl bromide	*p*-Nitrobenzyl bromide	Phenacyl bromide	*p*-Toluidine
Acetic - - - - - -	**112**	85	**78**	40	**153**
o-Acetylaminobenzoic - -	—	—	91	—	—
m-Acetylaminobenzoic - -	—	—	170	—	—
p-Acetylaminobenzoic - -	—	—	—	—	—
o-Acetylhydroxybenzoic - -	—	—	91	113	—
m-Acetylhydroxybenzoic -	—	—	140	—	—
p-Acetylhydroxybenzoic - -	—	—	—	—	—
Aconitic - - - - - -	—	186	—	90	—
Adipic - - - - - -	238	155	106	88	241
Allylmalonic - - - - -	—	—	46	—	—
o-Aminobenzoic - - - -	—	—	205	182	151
m-Aminobenzoic - - - -	140	—	200	—	—
p-Aminobenzoic - - - -	—	—	>250	—	—
α-Aminobutyric - - - -	—	—	223	—	—
p-Anisic - - - - - -	169	152	132	134	186
Anthranilic *see* o-*Aminobenzoic*					
Arachidic - - - - -	—	89	—	86	—
Asparaginic - - - - -	—	—	—	Gum	—
Azelaic - - - - - -	187	131	44	70	200
Benzilic - - - - - -	—	152	100	125	—
Benzoic - - - - - -	**164**	**119**	89	**119**	**158**
Benzylmalonic - - - -	—	—	120	—	—
Bromoacetic - - - - -	—	—	89	—	—
o-Bromobenzoic - - - -	—	102	110	83	—
m-Bromobenzoic - - - -	—	126	105	113	—
p-Bromobenzoic - - - -	—	134	140	87	—
Bromosuccinic - - - -	—	—	147	—	—
n-Butyric - - - - -	**96**	63	35	Oil	75
iso-Butyric - - - - -	105	77	Oil	—	107
Camphoric - - - - -	226	—	67	—	—

ACIDS, CARBOXYLIC (cont.)

	Aniline	*p*-Bromophenacyl bromide	*p*-Nitrobenzyl bromide	Phenacyl bromide	*p*-Toluidine
Capric *see Decanoic*					
Caproic *see Hexoic*					
Caprylic *see Octoic*					
Chloroacetic	137	105	—	—	—
o-Chlorobenzoic	118	**106**	106	**83**	—
m-Chlorobenzoic	124	117	107	116	—
p-Chlorobenzoic	194	126	130	87	—
Cinnamic	151	—	117	141	168
Citraconic	176	—	—	109	—
Citric	192	148	102	104	189
o-Coumaric	—	—	—	—	—
o-Cresotic	—	—	—	139	—
m-Cresotic	—	—	—	**117**	—
p-Cresotic	—	—	—	146	—
Decanoic	70	66	Oil	—	78
Dibromosuccinic	—	—	168	—	—
4 : 5-Dichlorophthalic	—	—	180	—	—
Diethylmalonic	—	—	91	—	—
2 : 4-Dihydroxybenzoic	127	—	—	—	—
Dimethylmalonic	—	—	84	—	—
2 : 4-Dinitrobenzoic	—	—	142	—	—
3 : 5-Dinitrobenzoic	—	—	157	—	—
Erucic	55	61	—	—	—
Ethyl glycollic	—	105	—	—	—
Ethylmalonic	—	—	75	—	—
Formic	**50**	140	31	Oil	53
Fumaric	314	—	151	198	—
Furoic	124	139	134	—	108

ACIDS, CARBOXYLIC (cont.)

	Aniline	*p*-Bromophenacyl bromide	*p*-Nitrobenzyl bromide	Phenacyl bromide	*p*-Toluidine
Gallic	207	—	—	Gum	—
Glutaric	224	137	69	104	218
Glycollic	–	138	107	—	143
n-Heptoic	65	72	—	Oil	80
n-Hexoic	92	72	—	—	73
Hippuric	—	151	136	—	—
Hydrocinnamic *see β-Phenylpropionic*					
o-Hydroxybenzoic	135	140	—	110	—
m-Hydroxybenzoic	156	168	—	146	163
p-Hydroxybenzoic	197	184	—	178	204
α-Hydroxy-*iso*-butyric	136	—	—	—	133
2-Hydroxy-3-naphthoic	249	—	—	—	222
o-Iodobenzoic	—	110	111	71	—
m-Iodobenzoic	—	128	121	116	—
p-Iodobenzoic	—	146	141	101d.	—
5-Iodo-2-hydroxybenzoic	—	–	—	—	—
Itaconic	—	117	91	80	—
Lactic	59	113	Oil	96	107
Lævulinic	102	84	61	—	109
Lauric	78	76.	—	49	87
Leucin	—	—	185	—	—
Lignoceric	—	91	—	88	—
Maleic	187	—	89	119	—
Malic	197	179	124	106	207
Malonic	225	Oil	86	Oil	—
Mandelic	—	—	—	85	—

ACIDS, CARBOXYLIC (cont.)

	Aniline	*p*-Bromophenacyl bromide	*p*-Nitrobenzyl bromide	Phenacyl bromide	*p*-Toluidine
Margaric	—	78	49	60	—
Methylethylmalonic	—	—	66	—	—
Mucic	—	—	>310	—	—
Myristic	84	81	—	56	93
o-Nitrobenzoic	155	101	112	125	—
m-Nitrobenzoic	154	137	142	106	162
p-Nitrobenzoic	211	134	169	128	203
o-Nitrocinnamic	—	142	132	126	—
m-Nitrocinnamic	—	178	174	146	—
p-Nitrocinnamic	—	191	187	146	—
3-Nitrophthalic	—	—	190	—	—
n-Nonic *see Pelargonic*					
n-Octoic	55	66	Oil	—	70
Oleic	41	46	—	Oil	43
Oxalic	246	242d.	204	Nil	268
Palmitic	89	84	43	58	98
Pelargonic	57	69	Oil	—	84
n-Pentadecanoic	78	77	40	54	—
Phenylacetic	118	89	65	—	136
Phenylalanine	—	—	222	—	—
Phenylpropiolic	128	—	83	—	142
β-Phenylpropionic	96	104	36	42	135
Phthalic	—	153	156	155	—
iso-Phthalic	—	179	264	191	—
tere-Phthalic	—	225	164	192	—
Pimelic	156	137	—	73	206
Piperic	—	—	145	—	—
Propionic	106	59	31	—	126
iso-Propylmalonic	—	—	81	—	—

ACIDS, CARBOXYLIC (cont.)

	Aniline	*p*-Bromophenacyl bromide	*p*-Nitrobenzyl bromide	Phenacyl bromide	*p*-Toluidine
Pyromucic *see Furoic*					
Pyrotartaric	—	—	—	102	—
Racemic *see* dl-*Tartaric*					
Saccharic	—	—	—	—	—
Salicylic *see* o-*Hydroxybenzoic*					
Sebacic	200	147	73	81	201
Sorbic	153	129	—	—	—
Stearic	94	90	—	69	102
Suberic	187	144	85	103	219
Succinic	228	211	88	148	255
dl-Tartaric	—	—	148	—	—
d-Tartaric	—	—	163	130	—
Thioglycollic	—	—	—	—	—
o-Toluic	125	57	91	75	144
m-Toluic	126	108	87	—	118
p-Toluic	144	153	104	103	160
n-Tridecanoic	80	75	—	46	88
n-Undecanoic	71	68	—	—	80
Uric	—	—	>305	—	—
n-Valeric	63	—	—	—	74
iso-Valeric	110	68	Oil	—	107
Vanillic	—	—	141	—	—

ALCOHOLS

	3:5-Dinitro-benzoyl chloride	3:5-Dinitrobenzoyl chloride and α-Naphthylamine	α-Naphthyl *iso*-cyanate	*p*-Nitrobenzoyl chloride	*p*-Nitrophenyl *iso*-cyanate	3-Nitrophthalic anhydride	Phenyl *iso*-cyanate	*p*-Xenyl *iso*-cyanate
Allyl alcohol	50	121	109	28	108	124	67	—
n-Amyl alcohol	46	85	68	Liquid	86	136	46	99
sec-Amyl alcohol (Methyl *n*-propyl carbinol)	62	—	—	—	—	103	—	—
sec-Amyl alcohol (Diethyl carbinol)	100	—	71	—	—	—	48	—
sec-Amyl alcohol (Methyl *iso*-propyl carbinol)	—	—	—	—	—	—	69	—
Amyl alcohol (*sec*-Butyl carbinol)	70	—	82	—	—	158	—	—
iso-Amyl alcohol (*iso*-Butyl carbinol)	62	105	68	—	98	166	55	—
tert-Amyl alcohol (Amylene hydrate)	118	124	72	85	—	—	—	—
Amylene hydrate *see* tert-*Amyl alcohol*								
Anisyl alcohol *see* p-*Methoxybenzyl alcohol*								
Benzhydrol	141	—	136	131	150	—	—	197
Benzoin	—	—	140	123	183	—	163	—
Benzyl alcohol	113	—	135	85	157	176	78	156
d-Borneol	154	—	131	153	—	—	138	—
iso-Borneol	—	—	130	129	—	—	—	—

ALCOHOLS (cont.)

	3:5-Dinitro-benzoyl chloride	3:5-Dinitrobenzoyl chloride and α-Naphthylamine	α-Naphthyl *iso*-cyanate	*p*-Nitrobenzoyl chloride	*p*-Nitrophenyl *iso*-cyanate	3-Nitrophthalic anhydride	Phenyl *iso*-cyanate	*p*-Xenyl *iso*-cyanate
n-Butyl alcohol	62	93	72	35	**96**	147	**60**	109
iso-Butyl alcohol	88	106	**100**	35	80	183	**86**	—
sec-Butyl alcohol	76	—	98	26	75	131	**65**	106
tert-Butyl alcohol	142	144	101	116	—	—	**140**	—
Capryl alcohol *see* sec-*Octyl alcohol*								
Cetyl alcohol	66	—	82	52	118	122	76	—
Cholesterol	—	—	160	190	205	—	168	—
Cinnamyl alcohol	121	—	114	78	—	—	91	—
Cyclohexanol	113	126	128	50	—	160	82	**144**
Cyclopentanol	—	—	118	—	—	—	132	—
n-Decyl alcohol	57	50	71	30	117	123	61	111
Diphenyl carbinol *see Benzhydrol*								
n-Dodecyl alcohol	60	—	80	45	117	124	74	113

Ethyl alcohol	94	121	*85*	**56**	129	**157**	52	119
Ethylene bromohydrin	—	—	87	—	—	—	76	—
Ethylene chlorohydrin	—	—	101	—	—	—	51	—
Ethylene glycol	169	—	176	140	—	—	**156**	—
Ethylene glycol monoethyl ether	75	—	67	—	80	118*	—	—
Ethylene glycol monomethyl ether	—	—	113	51	111	129	—	—
Fenchyl alcohol	—	—	148	—	—	—	104	—
Furfuryl alcohol	81	150	130	76	—	—	45	—
Geraniol	63	69	47	—	—	—	—	—
Glycerol	—	—	192	188	216	—	180	—
n-Heptadecyl alcohol	—	—	89	—	—	122	—	—
n-Heptyl alcohol	48	58	**60**	—	**105**	127	**59**	105
n-Hexyl alcohol	61	104	59	—	103	124	41	98
Lauryl alcohol *see* n-*Dodecyl alcohol*								
Linaloöl	—	—	53	70	—	—	65	—
Mannitol	—	—	—	—	—	—	303	—
l-Menthol	153	—	**120**	62	—	—	112	157
o-Methoxybenzyl alcohol	—	—	136	—	—	—	—	—
p-Methoxybenzyl alcohol	—	—	—	—	—	—	90	—

* Anhydrous

ALCOHOLS (cont.)

	3 : 5-Dinitro-benzoyl chloride	3 : 5-Dinitrobenzoyl chloride and α-Naphthylamine	α-Naphthyl *iso*-cyanate	*p*-Nitrobenzoyl chloride	*p*-Nitrophenyl *iso*-cyanate	3-Nitrophthalic anhydride	Phenyl *iso*-cyanate	*p*-Xenyl *iso*-cyanate
Methyl alcohol	109	**122**	124	**96**	180	153*	47	127
o-Methyl benzyl alcohol	—	—	—	—	—	—	79	—
m-Methyl benzyl alcohol	—	—	116	—	—	—	—	—
p-Methyl benzyl alcohol	—	—	—	—	—	—	79	—
2-Methyl cyclohexanol *cis-*	99	—	—	56	—	—	92	—
2-Methyl cyclohexanol *trans-*	115	—	—	65	—	—	105	—
3-Methyl cyclohexanol *cis-*	92	—	—	65	—	—	88	—
3-Methyl cyclohexanol *trans-*	98	—	—	58	—	—	94	—
4-Methyl cyclohexanol *cis-*	134	—	—	94	—	—	119	—
4-Methyl cyclohexanol *trans-*	140	—	157	67	—	—	125	—
Myristyl alcohol	—	—	—	—	—	123	71	—
n-Nonyl alcohol	52	—	—	—	104	125	62	115
n-Octadecyl alcohol	—	—	—	—	115	119	76	—
n-Octyl alcohol	62	49	66	Liquid	111	128	74	110
sec-Octyl alcohol	32	67	63	28	Oil	—	Oil	—

* Anhydrous

Pentadecyl alcohol	—	—	85	—	—	123	72	—
α-Phenyl *n*-butyl alcohol	—	—	99	58	—	—	—	—
α-Phenyl ethyl alcohol	94	—	106	43	—	—	94	—
β-Phenyl ethyl alcohol	108	—	119	62	135	123	79	—
α-Phenyl *n*-propyl alcohol	—	—	102	60	—	—	—	—
γ-Phenyl *n*-propyl alcohol	92	—	—	46	104	117	45	—
n-Propyl alcohol	75	104	79	35	115	142	51	129
iso-Propyl alcohol	122	144	106	110	116	153	88	138
Propylene glycol	—	—	—	—	—	—	153	—
Stearyl alcohol *see* n-*Octadecyl alcohol*								
Terpineol	79	94	147	139	—	—	112	—
Tetrahydrofurfuryl alcohol	84	—	—	47	—	—	58	—
Tridecyl alcohol	—	—	—	—	—	124	—	—
Trimethylene bromohydrin	—	—	74	—	—	—	—	—
Trimethylene chlorohydrin	—	—	76	—	—	—	—	—
Trimethylene glycol	178	—	164	119	—	—	137	—
n-Undecyl alcohol	—	—	—	—	100	123	52	106

ALDEHYDES

	Dimedone	Dimedone Anhydride	2 : 4-Dinitro-phenylhydrazine	Hydroxylamine hydrochloride	*p*-Nitro-phenylhydrazine	Phenyl-hydrazine	4-Phenyl-semicarbazide	Semicarbazide hydrochloride	*p*-Thiocyano-phenylhydrazine hydrochloride	Thio-semicarbazide
Acetaldehyde - - - - - -	140	174	168	47	128	63	151	163	—	146
Acrolein - - - - - - -	**192**	163	165	—	151	—	—	171	—	—
Aldol - - - - - - -	147	—	—	—	110	—	—	194	—	—
o-Aminobenzaldehyde - - - -	—	—	—	132	219	221	—	—	—	—
m-Aminobenzaldehyde - - - -	—	—	—	88	226	162	—	>280	—	—
p-Aminobenzaldehyde - - - -	—	—	—	124	—	175	—	173	—	—
Anisaldehyde *see* p-*Methoxybenzaldehyde*										
Benzaldehyde - - - - - -	**195**	200	237	35(α)	192	158	—	*ca.* *227*	135	160
m-Bromobenzaldehyde - - - -	—	—	—	—	220	141	—	205	127	—
n-Butyraldehyde - - - - -	134	—	126	—	91	—	135	**104**	—	—
iso-Butyraldehyde - - - - -	—	—	182	—	130	Oil	133	125	—	—
o-Chlorobenzaldehyde - - - -	205	225	206	—	249	86	—	—	160	—
m-Chlorobenzaldehyde - - - -	—	—	—	—	216	134	—	228	125	—
p-Chlorobenzaldehyde - - - -	—	—	—	—	239	127	+	231	149	—

Cinnamaldehyde	213	175	255	138	195	168	—	216	139	**135**
Citral	Nil	—	116	Oil	—	—	—	164	—	—
d-Citronellal	78	173	77	Oil	—	—	—	83	—	—
Crotonaldehyde	183	167	189	119	185	56	—	**201**	—	—
Cumaldehyde	171	173	243	58	190	129	—	210	140	—
n-Decaldehyde	92	—	104	69	—	—	109	102	—	100
2 : 4-Dihydroxybenzaldehyde	—	—	286d.	191	—	159	—	—	191	—
3 : 4-Dihydroxybenzaldehyde	145d.	—	275d.	150	—	—	—	—	—	—
2 : 4-Dimethoxybenzaldehyde	—	—	—	106	—	—	—	—	129	—
3 : 4-Dimethoxybenzaldehyde	—	—	262	95	—	121	—	177	117	—
p-Dimethylaminobenzaldehyde	193	—	325	—	182	148	—	—	158	—
2 : 4-Dinitrobenzaldehyde	—	—	258	128	—	228	—	—	—	—
n-Duodecaldehyde	—	—	106	77	90	—	—	106	—	100
Formaldehyde	189	171	168	Oil	182	Oil	—	169d.	—	—
Furfural	162	—	229	—	127	97	181	**203**	—	—
Glyoxal	186(m)	224(m)	327	—	302d.	170	—	>270	—	>300
n-Heptaldehyde	**103**	**112**	108	58	73	Oil	**133**	109	—	—
n-Hexaldehyde	109	—	104	51	80	—	135	106	—	—
p-Homosalicylaldehyde (OH = 1)	—	—	—	105	—	149	—	—	—	—
o-Hydroxybenzaldehyde	—	208	252	**57**	233	142	—	232	172	231

ALDEHYDES (cont.)

	Dimedone		2 : 4-Dinitro-phenylhydrazine	Hydroxylamine hydrochloride	*p*-Nitro-phenylhydrazine	Phenyl-hydrazine	4-Phenyl-semicarbazide	Semicarbazide hydrochloride	*p*-Thiocyano-phenylhydrazine hydrochloride	Thio-semicarbazide
	—	Anhydride								
m-Hydroxybenzaldehyde - - - -	—	—	260	88	222	130	—	*199*	167	—
p-Hydroxybenzaldehyde - - - -	189	246	280	—	*266*	177	—	224	154	224
o-Iodobenzaldehyde - - - - -	—	—	—	108	—	79	—	206	—	—
m-Iodobenzaldehyde - - - - -	—	—	—	63	213	155	—	226	—	—
p-Iodobenzaldehyde - - - - -	—	—	—	—	201	121	—	225	—	—
Lauryl aldehyde *see* n-*Duodecaldehyde*										
o-Methoxybenzaldehyde - - - -	—	—	253	92	205	—	—	215d.	147	—
p-Methoxybenzaldehyde - - - -	145	243	253	—	161	121	176	210	129	—
α-Naphthaldehyde - - - - -	—	—	—	98	237	80	—	222	—	—
β-Naphthaldehyde - - - - -	—	—	270	156	230	206	—	245	207	—
o-Nitrobenzaldehyde - - - - -	—	—	—	103	—	153	—	256	171	—

m-Nitrobenzaldehyde	—	—	—	118	—	120	194	246	161	163
p-Nitrobenzaldehyde	—	—	320	129	249	155	—	220	185	—
o-Nitrocinnamaldehyde	—	—	250	—	—	157	—	208	—	—
m-Nitrocinnamaldehyde	—	—	292	—	—	106	—	—	—	—
p-Nitrocinnamaldehyde	—	—	320	179	—	180	—	—	—	—
n-Nonaldehyde	86	—	96	63	—	—	131	—	—	77
n-Octaldehyde	90	—	106	59	80	—	128	98	—	94
Oenanthol *see* n-*Heptaldehyde*										
Phenylacetaldehyde	165	—	121	100	—	58	—	156	—	—
Piperonal	178	220	266	110	200	103	—	234	153	185
Propionaldehyde	155	143	155	—	124	Oil	130	—	—	159
Salicylaldehyde *see* o-*Hydroxybenzaldehyde*										
o-Tolualdehyde	—	—	194	49	222	—	—	224	—	—
m-Tolualdehyde	—	—	—	60	157	91	—	216	—	—
p-Tolualdehyde	—	—	234	80	200	113	—	234	118	—
2 : 4 : 6-Trinitrobenzaldehyde	—	—	208	—	247	202	—	214	—	—
n-Undecaldehyde	—	—	104	72	—	—	—	103	—	—
n-Valeraldehyde	105	—	98	52	—	—	126	—	—	65
iso-Valeraldehyde	155	173	123	48	110	Oil	—	132	—	53
Vanillin	197	228	271	117	229	105	—	*240d.*	*122*	197

ALKALOIDS

	Picric acid	Styphnic acid
Aconitine	166	120
Atropine	176	180
Brucine	280	266
Caffeine	*145*	**199**
Cinchonidine	209	—
Cinchonine	194	106
Cocaine	155	187
Codeine	197	115
Coniine	75	—
Dionine	—	155
Heroine	205	222
Hyoscine	188	—
Hyoscyamine	165	—
Morphine	228	189
Narceine	195	—
Narcotine	141	—
Nicotine	218	190
Papaverine	—	—
Pilocarpine	147	183
Piperine	—	—
Quinidine	—	149
Quinine	132	**154**
Scopolamine	174	—
Sparteine	206	—
Strychnine	286	266
Theobromine	—	*chars*

AMIDES

	Xanthydrol
Acetamide	245
iso-Amyl carbamate	145
Benzamide	224
Biuret	—
iso-Butyl carbamate	148
n-Butyramide	186
iso-Butyramide	211
Chloroacetamide	209
Cyanoacetamide	223
Dichloroacetamide	Nil
Dicyandiamide	Nil
asym-Dimethyl urea	225
asym-Diphenyl urea	180
Ethyl carbamate	169
Formamide	184
Furoamide	210
n-Heptamide	154
n-Hexamide	160
iso-Hexamide	160
Malonamide	270
Methyl carbamate	193
Methyl urea	230

AMIDES (cont.)

	Xanthydrol
p-Nitrobenzamide	232
n-Octamide	148
Oxamide	Nil
Palmitamide	141
Phenylacetamide	196
α-Phenyl butyramide	158
β-Phenyl propionamide	189
Phenyl urea	225
Phthalimide	177
Propionamide	214
Salicylamide	Nil
Stearamide	140
Succinamide	275
Succinimide	246
o-Toluamide	200
p-Toluamide	225
o-Tolyl urea	228
p-Tolyl urea	—
Trichloroacetamide	Nil
Urea	*274*
Urethane *see Ethyl carbamate*	
n-Valeramide	167
iso-Valeramide	183

AMINES, PRIMARY ALIPHATIC

	Benzene sulphonylchloride	Benzoyl chloride	2 : 4-Dinitro-chlorobenzene	α-Naphthyl *iso*-cyanate	α-Naphthyl *iso*-thiocyanate	*p*-Nitrophenyl *iso*-cyanate	Phenyl *iso*-thiocyanate	Phthalic anhydride	Picric acid	Picryl chloride	*p*-Toluene sulphonylchloride	2 : 4 : 5-Trinitrotoluene
Allylamine	40	Liq.	76	—	—	—	100	70	140	80	—	—
Aminoacetic acid *see Glycine*												
n-Amylamine	—	—	—	—	103	—	69	—	—	—	—	99
iso-Amylamine	—	—	—	132	97	—	102	—	—	—	65	87
Benzylamine	**88**	**106**	*116*	203	172	—	147	**115**	*199*	**142**	**116**	**100**
n-Butylamine	Liq.	—	—	—	109	146	65	34	151	—	—	96
iso-Butylamine	—	57	80	—	137	—	82	93	—	95	78	112
sec-Butylamine	71	—	—	—	—	—	—	—	140	—	—	—
tert-Butylamine	—	—	—	—	—	—	—	—	—	—	—	—
Cyclohexylamine	—	147	**156**	—	142	170	—	168	—	—	—	*138*
Ethanolamine	—	—	—	—	—	—	—	127	160	—	—	*118*
Ethylamine	—	69	113	**200**	**121**	158	**106**	78	168	84	62	**126**
Ethylenediamine	168	249	—	—	—	—	102	—	233	230	160	280

AMINES, PRIMARY ALIPHATIC (cont.)

	Benzene sulphonylchloride	Benzoyl chloride	2 : 4-Dinitro-chlorobenzene	α-Naphthyl *iso*-cyanate	α-Naphthyl *iso*-thiocyanate	*p*-Nitrophenyl *iso*-cyanate	Phenyl *iso*-thiocyanate	Phthalic anhydride	Picric acid	Picryl chloride	*p*-Toluene sulphonylchloride	2 : 4 : 5-Trinitrotoluene
Glycine	—	187	—	—	—	—	—	—	—	161	—	—
n-Heptylamine	Oil	—	—	—	—	—	—	40	121	—	—	50
Hexamethylenediamine	—	—	—	—	—	—	124	—	—	—	—	—
n-Hexylamine	—	—	—	—	79	—	77	—	—	—	—	—
iso-Hexylamine	—	—	—	—	79	—	112	—	—	—	—	—
Methylamine	—	80	178	197	—	—	—	134	215	111	77	173
Pentamethylenediamine	—	—	—	—	—	—	148	—	—	—	—	—
β-Phenylethylamine	—	114	—	—	—	—	135	130	167	—	—	—
n-Propylamine	36	85	—	—	103	151	63	66	135	—	52	101
iso-Propylamine	26	—	—	—	143	—	—	86	—	—	—	—
Tetramethylenediamine	—	—	—	—	—	—	168	—	—	—	—	—

AMINES, PRIMARY AROMATIC

Bis derivatives are quoted for aminophenols and diamines

	Acetic anhydride	Benzaldehyde	Benzene sulphonylchloride	Benzoyl chloride	2 : 4-Dinitro-chlorobenzene	Formic acid	*p*-Nitro-benzaldehyde	Phenyl *iso*-thiocyanate	Phthalic anhydride	Picric acid	Picryl chloride	*p*-Toluene sulphonylchloride	1 : 3 : 5-Trinitrobenzene
p-Aminoacetanilide - - -	303	—	—	—	—	—	—	—	283	—	—	—	—
o-Aminoacetophenone - -	76	—	—	80	—	76	—	—	—	—	232	148	—
p-Aminoacetophenone - - -	167	96	128	205	—	—	—	—	—	—	163	203	137
p-Aminoazobenzene - - - -	145	130	—	211	—	162	182	—	—	—	177	—	—
o-Aminobenzoic acid - - -	185	127	214	181	—	168	166	—	217	—	272	217	193
m-Aminobenzoic acid - - -	249	119	—	—	—	225	247	—	—	—	234	—	Nil
p-Aminobenzoic acid - - -	251	193	—	278	—	268	276	—	—	—	293	—	151
p-Aminodiethylaniline - - -	104	—	—	172	—	—	142	—	260	—	—	—	79
p-Aminodimethylaniline - - -	131	98	—	228	—	108	219	—	—	186	—	—	—
p-Aminodiphenylamine - - -	158	108	—	203	190	—	172	—	—	—	—	—	—
2-Amino-1-naphthol - - - -	116	—	—	180	—	—	187	—	—	—	—	—	—
4-Amino-1-naphthol - - - -	158	137	—	215	—	168	171	—	—	—	—	—	—
5-Amino-1-naphthol - - - -	—	—	—	276	—	—	—	—	—	—	—	—	—
1-Amino-2-naphthol - - - -	206	129	—	230	—	204	174	—	—	110	—	—	—
3-Amino-2-naphthol - - - -	188	—	—	—	—	—	—	—	—	—	—	—	—

AMINES, PRIMARY AROMATIC (cont.)

	Acetic anhydride	Benzaldehyde	Benzene sulphonylchloride	Benzoyl chloride	2 : 4-Dinitro-chlorobenzene	Formic acid	*p*-Nitro-benzaldehyde	Phenyl *iso*-thiocyanate	Phthalic anhydride	Picric acid	Picryl chloride	*p*-Toluene sulphonylchloride	1 : 3 : 5-Trinitrobenzene
5-Amino-2-naphthol - - - - -	187	—	—	223	—	—	—	—	—	170	—	—	—
7-Amino-2-naphthol - - - - -	156	—	—	187	—	—	—	—	—	—	—	—	—
8-Amino-2-naphthol - - - - -	—	—	—	208	—	—	—	—	—	—	—	—	—
o-Aminophenol - - - - -	124	89	141(m)	184	**199**(m)	129	160	—	—	—	175	139(m)	—
m-Aminophenol - - - - -	101	—	—	153	—	—	—	—	—	—	204	157(m)	—
p-Aminophenol - - - - -	150	182	154(m)	234	—	140	168	150	—	—	174	143(m)	—
2-Aminopyridine - - - - -	71	—	—	165	—	—	—	—	—	*223*	—	—	—
2-Aminoquinoline - - - - -	—	—	—	—	—	—	—	—	—	255	—	—	186
3-Aminoquinoline - - - - -	167	—	—	—	—	—	—	—	—	210	—	—	—
4-Aminoquinoline - - - - -	176	—	—	—	—	—	—	—	—	274	—	—	111
5-Aminoquinoline - - - - -	178	—	—	—	211	—	—	—	—	—	—	204	—
6-Aminoquinoline - - - - -	138	—	—	169	217	—	—	—	—	—	—	195	—
7-Aminoquinoline - - - - -	167	—	—	189	204	—	—	—	—	—	—	—	—
8-Aminoquinoline - - - - -	103	—	—	98	266	—	—	—	—	—	—	155	—
Aniline - - - - - - -	**114**	**54**	110	**163**	**156**	**47**	93	**154**	208	165	178	**103**	123
Anisidine *see Methoxyaniline*													
Anthranilic acid *see* o-*Aminobenzoic acid*													

Benzidine	**317**	**238**	235	352	—	*Sublimes*	242	—	—	—	—	243	—
o-Bromoaniline	99	—	—	116	—	87	*122*	146	—	129	*192*	—	128
m-Bromoaniline	88	—	—	120	—	63	—	97	—	180	—	—	116
p-Bromoaniline	**167**	67	134	202	—	119	**163**	**158**	203	180	**188**	—	113
4-Bromo-1-naphthylamine	193	—	149	—	—	172	—	—	—	—	—	—	196
1-Bromo-2-naphthylamine	140	94	—	—	—	—	155	—	—	178	—	—	192
m-Bromo-*p*-toluidine ($CH_3 = 1$)	118	—	—	149	—	—	—	154	—	—	—	—	—
o-Chloroaniline	88	34	130	99	—	77	**126**	156	—	134	**169**	—	135
m-Chloroaniline	**73**	Oil	121	**122**	—	58	—	116	—	177	138	**138**	115
p-Chloroaniline	**178**	62	121	193	—	102	*135*	152	195	178	**173**	**95**	111
4-Chloro-1-naphthylamine	184	—	—	—	—	—	—	—	—	—	—	—	—
1-Chloro-2-naphthylamine	147	—	131	99	—	—	—	—	—	174	—	—	183
5-Chloro-*o*-toluidine ($CH_3 = 1$)	140	—	125	—	—	—	—	—	—	—	—	—	—
6-Chloro-*m*-toluidine	91	—	130	119	—	—	—	—	—	—	—	—	—
3-Chloro-*p*-toluidine	118	—	110	138	—	—	—	—	—	—	—	—	—
p-Cumidine	103	—	—	162	—	—	—	—	—	—	—	—	—
pseudo-Cumidine	162	—	137	167	—	121	—	—	148	—	—	—	—
o-Dianisidine	**243**	—	—	236	—	—	—	—	—	225	—	—	144
2 : 4-Dibromoaniline	146	67	—	134	—	146	—	171	154	124	—	—	86
2 : 5-Dibromoaniline	172	—	—	—	—	—	—	172	—	—	—	—	—
2 : 6-Dibromoaniline	210	—	—	—	—	—	—	—	—	124	—	—	104
3 : 5-Dibromoaniline	231	—	—	169	—	100	—	163	—	—	—	—	—

AMINES, PRIMARY AROMATIC (cont.)

	Acetic anhydride	Benzaldehyde	Benzene sulphonylchloride	Benzoyl chloride	2 : 4-Dinitro-chlorobenzene	Formic acid	*p*-Nitro-benzaldehyde	Phenyl *iso*-thiocyanate	Phthalic anhydride	Picric acid	Picryl chloride	*p*-Toluene sulphonylchloride	1 : 3 : 5-Trinitrobenzene
1 : 6-Dibromo-2-naphthylamine	212	—	—	—	—	—	—	—	—	131	—	—	165
2 : 4-Dichloroaniline	146	—	128	117	—	153	—	—	180	106	—	—	91
Diethyl-*p*-phenylenediamine *see* p-*Aminodiethylaniline*													
Dimethyl-*p*-phenylenediamine *see* p-*Aminodimethylaniline*													
2 : 4-Dinitroaniline	120	133	—	220	—	—	—	—	—	—	—	—	—
o-Ethoxyaniline	79	Oil	—	104	164	62	81	—	—	—	137	164	—
m-Ethoxyaniline	96	—	—	103	—	52	—	—	—	158	—	157	—
p-Ethoxyaniline	134	76	142	173	118	69	126	—	—	—	124	106	—
o-Iodoaniline	110	—	—	—	—	—	—	—	—	112	—	—	—
m-Iodoaniline	119	—	—	157	—	—	—	—	—	—	—	128	—
p-Iodoaniline	181	86	—	210	—	109	—	153	228	—	—	—	108
Mesidine	216	43	—	204	—	176	—	—	171	190	—	—	—

o-Methoxyaniline	85	—	89	60	151	83	111	—	—	—	**136**	127	98
m-Methoxyaniline	80	—	—	—	—	57	—	—	—	169	—	68	—
p-Methoxyaniline	**127**	62	**96**	153	141	81	*135*	171	—	—	**165**	114	82
α-Naphthylamine	**160**	73	**171**	**161**	190	139	*158*	157	181	161	198	**157**	214
β-Naphthylamine	**134**	102	98	162	179	128	121	157	216	195	232	**133**	162
1 : 2-Naphthylenediamine	234	—	—	291	—	—	—	—	—	—	—	—	204
1 : 4-Naphthylenediamine	303	—	—	280	—	—	—	—	—	—	—	—	218
o-Nitroaniline	**93**	—	104	98	—	122	—	—	203	73	ca 220	—	91
m-Nitroaniline	**154**	73	136	155	—	**134**	152	155	243	143	205	**138**	98
p-Nitroaniline	**216**	115	139	197	—	194	198	—	268	100	216	**191**	Nil
2-Nitro-1-naphthylamine	199	—	—	174	—	—	—	—	—	—	—	—	—
3-Nitro-1-naphthylamine	255	122	—	220	—	216	242	—	—	—	—	200	—
4-Nitro-1-naphthylamine	190	—	158	224	—	—	—	—	—	—	—	185	—
5-Nitro-1-naphthylamine	220	—	183	—	—	199	—	—	—	—	—	—	—
8-Nitro-1-naphthylamine	191	—	194	—	—	—	—	—	—	—	—	—	—
1-Nitro-2-naphthylamine	124	—	156	168	—	Nil	—	—	—	—	—	161	116
4-Nitro-2-naphthylamine	—	—	—	—	—	205	—	—	—	—	—	—	—
5-Nitro-2-naphthylamine	186	—	—	182	—	—	—	—	—	—	—	—	—
3-Nitro-*o*-toluidine ($CH_3 = 1$)	158	—	—	—	—	Nil	—	—	—	—	—	—	—
4-Nitro-*o*-toluidine	**151**	116	172	**183**	—	**186**	227	—	232	—	—	—	—
5-Nitro-*o*-toluidine	202	—	158	—	—	*162*	—	—	—	—	—	174	—
6-Nitro-*o*-toluidine	158	—	—	167	—	—	—	—	—	—	—	—	—
6-Nitro-*m*-toluidine	102	—	—	—	—	—	—	—	—	—	—	—	—
2-Nitro-*p*-toluidine	93	78	161	172	—	134	—	—	222	—	—	—	—

AMINES, PRIMARY AROMATIC (cont.)

	Acetic anhydride	Benzaldehyde	Benzene sulphonylchloride	Benzoyl chloride	2 : 4-Dinitro-chlorobenzene	Formic acid	*p*-Nitro-benzaldehyde	Phenyl *iso*-thiocyanate	Phthalic anhydride	Picric acid	Picryl chloride	*p*-Toluene sulphonylchloride	1 : 3 : 5-Trinitrobenzene
3-Nitro-*p*-toluidine	**92**	—	99	**143**	—	*125*	161	—	—	—	—	100	—
Phenetidine *see* ***Ethoxyaniline***													
o-Phenylenediamine	186	106	—	301	—	**170**	*>280*	—	165	208	178	202	—
m-Phenylenediamine	190	105	—	240	—	155	—	—	154	184	207	172	—
p-Phenylenediamine	303	140	247	>300	**177**	206	—	—	285	—	186	266	—
ar-Tetrahydro-α-naphthylamine	158	—	—	—	134	—	—	—	—	—	—	—	113
ar-Tetrahydro-β-naphthylamine	107	—	—	167	121	—	—	—	—	—	—	—	—
o-Tolidine	315	**152**	—	265	—	254	—	—	—	**185**	—	—	128
o-Toluidine	**109**	Oil	124	**144**	120	59	89	136	183	200	**168**	**110**	126
m-Toluidine	**66**	Oil	**83**	125	159	Oil	*100*	**91**	176	**195**	**127**	114	—
p-Toluidine	**145**	Oil	120	**158**	**136**	53	122	141	202	169	**164**	**118**	—
m-Tolylenediamine	224	—	192	224	—	—	—	—	—	—	—	—	—
p-Tolylenediamine	220	—	—	307	—	—	—	—	—	—	—	—	—
2 : 4 : 6-Tribromoaniline	232	—	—	198	—	222	—	—	—	—	—	—	111
2 : 4 : 6-Trichloroaniline	206	—	—	174	—	180	—	—	—	83	—	—	94

2 : 4 : 6-Trinitroaniline	ca230	—	—	196	—	—	—	—	—	—	—	—	—
o-Xenylamine	118	—	—	86	—	75	—	—	—	—	—	—	—
p-Xenylamine	**175**	*149*	—	**233**	—	**175**	—	—	—	—	*175*	—	—
3-*o*-Xylidine	134	—	—	—	—	—	—	—	—	—	—	—	—
4-*o*-Xylidine	99	—	118	—	141	52	—	—	—	—	179	154	—
2-*m*-Xylidine	177	Oil	—	168	—	165	—	—	204	—	212	—	—
4-*m*-Xylidine	130	Oil	130	192	156	114	88	134	155	209	159	—	—
5-*m*-Xylidine	144	—	—	—	—	77	—	—	135	—	—	—	—
2-*p*-Xylidine	139	101	**139**	140	—	117	—	—	163	171	163	119	—

AMINES, SECONDARY

	Acetic anhydride	Benzene sulphonylchloride	Benzoyl chloride	2 : 4-Dinitro-chlorobenzene	Formic acid	α-Naphthyl *iso*-cyanate	α-Naphthyl *iso*-thiocyanate	*p*-Nitrophenyl *iso*-cyanate	Picric acid	Picryl chloride	*p*-Toluene sulphonylchloride	1 : 3 : 5-Tri-nitrobenzene
Benzylaniline	58	119	107	—	48	—	—	—	—	—	—	92
Benzyl α-naphthylamine	—	—	—	—	—	—	—	—	—	—	—	174
Benzyl β-naphthylamine	—	—	115	—	—	—	—	—	141	—	—	141
n-Butyl aniline	Liq.	—	—	—	—	—	—	—	—	—	—	—
Di-*iso*-amylamine	—	—	—	—	—	95	118	—	—	—	—	—
Dibenzylamine	—	68	—	—	52	—	131	—	—	173	—	—
Di-*n*-butylamine	—	—	—	—	—	—	123	—	60	—	—	—
Di-*iso*-butylamine	—	—	—	—	—	119	—	—	—	—	—	—
Diethanolamine	—	—	—	—	—	—	—	—	101	*147*	—	—
Diethylamine	Liq.	42	Liq.	80	Liq.	**128**	108	**162**	Nil	164	60	—
Dimethylamine	Liq.	47	42	87	Liq.	159	168	221	155	138	79	—
αα-Dinaphthylamine	217	—	—	—	—	—	—	—	169	—	—	157
αβ-Dinaphthylamine	—	—	—	—	—	—	—	—	173	—	—	—
ββ-Dinaphthylamine	—	—	—	—	—	—	—	—	165	—	—	174
Diphenylamine	**101**	122	180	—	**74**	—	—	—	182	63	**142**	100
Di-*n*-propylamine	—	—	—	—	—	93	161	130	75	—	—	—
Di-*iso*-propylamine	—	—	—	—	—	—	—	—	140	—	—	—

Ethylaniline	54	—	60	—	Liq.	—	—	—	132	106	**88**	56
Ethyl α-naphthylamine	—	—	—	—	—	—	—	—	—	—	—	154
Ethyl β-naphthylamine	49	—	—	—	—	—	—	—	—	—	—	106
Ethyl *o*-toluidine	Liq.	—	—	114	—	—	—	—	—	—	—	—
Ethyl *m*-toluidine	Liq.	—	—	—	—	—	—	—	—	132	—	—
Ethyl *p*-toluidine	—	—	—	120	—	—	—	—	—	—	71	—
Indole	—	—	68	—	52	—	—	—	—	—	—	187
Methylaniline	101	78	63	—	Liq.	—	—	—	147	129	**95**	82
Methyl α-naphthylamine	98	—	121	—	—	—	—	—	—	—	—	—
Methyl *o*-toluidine	56	—	66	155	—	—	—	—	90	165	—	—
Methyl *m*-toluidine	77	—	—	—	—	—	—	—	—	—	—	—
Methyl *p*-toluidine	83	—	—	—	—	—	—	—	131	145	—	—
Morpholine	—	—	75	—	—	—	—	—	146	—	147	—
Phenyl α-naphthylamine	115	—	152	—	—	—	—	—	—	—	—	130
Phenyl β-naphthylamine	93	—	148	—	—	—	—	—	—	—	—	116
Piperazine	134	282	191	—	—	—	—	—	280	—	—	—
Piperidine	Liq.	93	48	—	Liq.	—	—	164	152	97	—	—
***n*-Propylaniline**	48	54	—	—	Liq.	—	—	—	—	—	—	—
Pyrrol	Liq.	—	Liq.	—	—	—	—	280	69	—	—	—
Skatole	—	—	—	—	—	—	—	—	171	—	—	—
Tetrahydroquinoline	Liq.	67	75	—	—	—	—	—	—	—	—	100
***p*-Tolyl α-naphthylamine**	124	—	—	—	—	—	—	—	—	—	—	—
***p*-Tolyl β-naphthylamine**	85	—	—	—	—	—	—	—	—	—	—	—

AMINES, TERTIARY

	Methyl iodide	Picric acid	Styphnic acid	1 : 3 : 5-Trinitrobenzene
Acridine	**224**	—	—	115
2-Aminoquinoline	247	256	—	186
4-Aminoquinoline	224	274	—	—
6-Aminoquinoline	199	—	239	—
Benzylethylaniline	161	111	—	—
Benzylmethylaniline	164	127	—	—
Dibenzylaniline	135	131	—	—
Diethylaniline	102	142	—	42
Diethyl α-naphthylamine	—	—	—	95
Diethyl β-naphthylamine	—	—	—	116
Diethyl *o*-toluidine	224	—	—	—
Diethyl *p*-toluidine	184	—	—	—
p-Dimethylaminobenzaldehyde	—	—	—	91
Dimethylaniline	228	**162**	—	109
Dimethyl α-naphthylamine	—	145	—	106
Dimethyl β-naphthylamine	—	200	—	—
Dimethyl *o*-toluidine	—	122	—	—
Dimethyl *m*-toluidine	177	—	—	—
Dimethyl *p*-toluidine	220	130	—	124
8-Hydroxyquinoline	143	204	193	—
2 : 3-Lutidine	—	184	—	—
2 : 4-Lutidine	—	**179**	—	—
2 : 5-Lutidine	—	165	—	—
2 : 6-Lutidine	**238**	**161**	—	—
3 : 4-Lutidine	—	163	—	—
3 : 5-Lutidine	—	229	—	—
Methylethylaniline	125	134	—	—

AMINES, TERTIARY (cont.)

	Methyl iodide	Picric acid	Styphnic acid	1:3:5-Trinitrobenzene
2-Methylquinoline	195	191	213	—
3-Methylquinoline	221	187	—	—
4-Methylquinoline	174	212		—
5-Methylquinoline	105	213	—	—
6-Methylquinoline	219	229	201	—
7-Methylquinoline	—	237	-	—
8-Methylquinoline	—	200	218	—
α-Naphthoquinoline	179	192	- -	134
β-Naphthoquinoline	205	259	—	112
α-Picoline	*230*	169	180	—
β-Picoline	–	150	153	—
γ-Picoline	*152*	**167**	–	—
Pyridine	117	167	185	—
Quinaldine *see 2-Methylquinoline*				
Quinoline	**72**	**203**	207	—
iso-Quinoline	159	**222**	-	—
Tetramethyl-*p*-phenylenediamine	–	—	--	142
Tri-*n*-amylamine	—	—	—	- -
Tribenzylamine	184	190	–	—
Tri-*n*-butylamine	180	—	- -	—
Triethanolamine	- -	—	—	—
Triethylamine	—	173	—	—
Trimethylamine	230	216	—	—
Tri-*n*-propylamine	–	117	—	—
2 : 4 : 6-Trimethylpyridine	--	**156**	—	—
2 : 3 : 6-Trimethylpyridine	—	143	—	—
2 : 4 : 5-Trimethylpyridine	-	131	—	—

BARBITURIC ACIDS

	p-Nitrobenzyl bromide	Xanthydrol
5-Allyl-5-*n*-butyl barbituric acid	169	240
5-Allyl-5-ethyl barbituric acid	196	242
5-Allyl-5-phenyl barbituric acid	152	223
5-Allyl-5-*iso*-propyl barbituric acid	192	227
5-Amyl-5-ethyl barbituric acid	131	—
5-*iso*-Amyl-5-ethyl barbituric acid (Amytal)	138	251
5-Bromopropenyl-5-*sec*-butyl barbituric acid	192	—
5-Bromopropenyl-5-*iso*-propyl barbituric acid (Noctal)	201	—
5-*n*-Butyl barbituric acid	180	—
5-*n*-Butyl-5-ethyl barbituric acid (Neonal)	146	250
5-*iso*-Butyl-5-ethyl barbituric acid	—	260
5-Cyclohexenyl-5-ethyl barbituric acid (Phanodorm)	199	257
5 : 5-Diallyl barbituric acid (Dial)	190	243
5 : 5-Diethyl barbituric acid (Veronal)	194	246
1 : 3-Diphenyl-5-ethyl barbituric acid	218	Nil
5 : 5-Di-*n*-propyl barbituric acid	182	269
5-Ethyl barbituric acid	214	—
5-Ethyl-5-phenyl barbituric acid (Luminal)	182	219
5-Ethyl-5-*iso*-propyl barbituric acid	160	—
5-Methyl barbituric acid	208	—
1-Methyl-5-cyclohexenyl-5-methyl barbituric acid (Epivan)	115	—
3-Methyl-5 : 5-diethyl barbituric acid (*N*-Methyl veronal)	104	—
1-Methyl-5-ethyl-5-phenyl barbituric acid (Prominal)	115	—
5-Methyl-5-hexyl barbituric acid	139	—
5-Methyl-5-phenyl barbituric acid	197	282
3-Phenyl-5 : 5-diethyl barbituric acid (*N*-Phenyl veronal)	133	—
5-*iso*-Propyl barbituric acid	187	208
3 : 5 : 5-Triethyl barbituric acid (*N*-Ethyl veronal)	69	—

ETHERS

	Picric acid	1:3:5-Trinitrobenzene
iso-Amyl α-naphthyl ether	96	—
iso-Amyl β-naphthyl ether	94	—
Anisole	81	—
n-Butyl α-naphthyl ether	85	—
n-Butyl β-naphthyl ether	67	—
iso-Butyl α-naphthyl ether	105	—
iso-Butyl β-naphthyl ether	84	—
sec-Butyl α-naphthyl ether	101	—
sec-Butyl β-naphthyl ether	86	—
Dibenzyl ether	78	—
Diphenyl ether	110	—
Ethyl α-naphthyl ether	119	126
Ethyl β-naphthyl ether	101	95
o-Methyl anisole	119	—
m-Methyl anisole	114	—
p-Methyl anisole	89	—
Methyl α-naphthyl ether	130	138
Methyl β-naphthyl ether	117	94
Phenetole	92	—
n-Propyl α-naphthyl ether	99	—
n-Propyl β-naphthyl ether	81	—
iso-Propyl α-naphthyl ether	105	—
iso-Propyl β-naphthyl ether	95	—
Safrole	105	51
iso-Safrole	75	86

HALIDES

The anilides and α-naphthalides included in this table are those which have actually been prepared from the halides and *iso*-cyanates, but other anilides will be found in the carboxylic acid table (p. 110).

	α-Naphthyl *iso*-cyanate	Phenyl *iso*-cyanate
Allyl - - - - - - -	—	114*
n-Amyl - - - - - - -	—	**92**
Amyl (2-methyl-*n*-butyl) - -	—	88
iso-Amyl - - - - - -	111	110
sec-Amyl (1-methyl-*n*-butyl) - -	103	87
sec-Amyl (1-ethyl-*n*-propyl) - -	117	125
tert-Amyl - - - - - -	138	91
Benzyl - - - - - - -	166	117
n-Butyl - - - - - - -	**109**	**63**
iso-Butyl - - - - - -	126	110
sec-Butyl - - - - - -	129	107
tert-Butyl - - - - - -	147	130
p-Chlorobenzyl - - - - -	—	166
Cyclohexyl - - - - - -	188	**146**
Ethyl - - - - - - -	126	104
n-Heptyl - - - - - -	—	55
n-Hexyl - - - - - - -	—	65
2-*n*-Hexyl - - - - - -	—	92
Methyl - - - - - - -	160	113
α-Naphthyl (*see also p.* 144) - -	236	—
dl-2-Octyl - - - - - -	—	73
d-2-Octyl - - - - - -	—	73
Phenyl - - - - - - -	161	—
n-Propyl - - - - - -	—	**96**
iso-Propyl - - - - - -	—	104
Styryl - - - - - - -	217	—
p-Tolyl - - - - - - -	173	—

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* The anilide of crotonic acid, not of vinylacetic acid, is obtained from allyl halides.

HETEROCYCLIC COMPOUNDS

	Picric acid	Styphnic acid	1:3:5-Trinitrobenzene
Antipyrine - - - -	181	—	—
Carbazole - - - -	**182**	**179**	**200**
Coumarone - - - -	103	—	104
Diphenylene oxide - - -	—	—	96
Indole *see p.* 137			
1-Phenyl-3-methyl pyrazolone-5	—	—	92
1-Phenyl pyrazolone-5 - -	—	—	198
Skatole *see p.* 137			

HYDROCARBONS, AROMATIC

	Phthalic anhydride	Picric acid	Styphnic acid	1:3:5-Trinitrobenzene
Acenaphthene	**199**	161	**154**	**168**
Acenaphthylene	—	201	—	221
Anthracene	—	**138**	**180**	**164**
Benzene	128	—	—	—
α-Benzyl naphthalene	—	101	134	—
β-Benzyl naphthalene	—	93	—	—
α-Bromonaphthalene	—	134	118	137
n-Butyl benzene	99	—	—	—
α-Chloronaphthalene	—	137	128	—
Chrysene	214	273	—	**186**
Cumene	133	—	—	—
pseudo-Cumene	—	—	—	—
p-Cymene	124	—	—	—
Dibenzyl	—	Nil	Nil	102
1 : 6-Dimethyl naphthalene	—	114	—	—
1 : 7-Dimethyl naphthalene	—	121	—	—
2 : 3-Dimethyl naphthalene	—	124	—	—
2 : 6-Dimethyl naphthalene	—	143	—	—
2 : 7-Dimethyl naphthalene	—	136	—	—
Diphenyl	225	Nil	Nil	—
Diphenyl acetylene	—	111	—	96
Durene	264	—	—	—
Ethyl benzene	*128*	—	—	—
α-Ethyl naphthalene	—	98	—	—
β-Ethyl naphthalene	—	71	—	—
Fluoranthene	—	**182**	*151*	***207***
Fluorene	228	84	*134*	**105**

HYDROCARBONS, AROMATIC (cont.)

	Phthalic anhydride	Picric acid	Styphnic acid	1:3:5-Trinitrobenzene
Hemimellitene	—	—	—	—
Hexamethyl benzene	—	170	—	174
Indene	—	96	—	101
Mesitylene	212	—	—	—
α-Methyl naphthalene	—	141	—	—
β-Methyl naphthalene	—	**115**	—	123
Naphthacene	—	—	—	—
Naphthalene	173	**150**	**168**	**153**
Naphthanthracene	—	133	—	—
Pentamethyl benzene	—	131	—	121
Phenanthrene	—	**143**	*142*	*164*
Picene	—	—	—	—
Prehnitene	—	90	—	—
n-Propyl benzene	126	—	—	—
iso-Propyl benzene *see Cumene*				
Pyrene	—	227	—	245
Retene	—	**123**	**141**	**139**
Stilbene	—	—	142	120
Styrene	—	—	—	—
Tetralin	**154**	—	—	—
Toluene	**138**	—	—	—
o-Xylene	*129d*	—	—	—
m-Xylene	126	—	—	—
p-Xylene	132	—	—	—

KETONES

	Benzaldehyde	2 : 4-Dinitro-phenylhydrazine	Hydroxylamine hydrochloride	*p*-Nitro-phenylhydrazine	Phenyl-hydrazine	4-Phenyl-semicarbazide	Semicarbazide hydrochloride	*p*-Thiocyano-phenylhydrazine hydrochloride	Thio-semicarbazide
2-Aceto-1-naphthol - - - - -	126	—	169	*264*	136	—	—	211	—
Acetone - - - - - -	112	126	60	148	42	—	188	129	179
Acetonyl acetone - - - - -	—	257	134	—	—	—	—	—	—
Acetophenone - - - - -	58	249	59	184	105	—	**198**	109	108
Acetyl acetone - - - - -	Oil (m)	209	149	—	—	—	—	—	—
p-Aminoacetophenone - - - -	—	—	—	—	—	—	—	156	—
Benzal acetone - - - - -	112	227	115	166	156	—	186	—	148
Benzal acetophenone - - - -	Nil	244	—	—	118	—	—	—	—
Benzil - - - - - - -	—	189	237	290	225	—	244d.	—	—
Benzoin - - - - - -	—	246	151	—	106	—	206d.	—	—
Benzophenone - - - - -	—	238	142	154	**138**	—	165	—	—
Benzoyl acetone - - - - -	99(m)	151	—	101	—	—	—	—	—
p-Bromoacetophenone - - - -	—	230	—	—	126	—	—	157	—
d-Camphor - - - - - -	98	177	118	*217*	233	—	237	—	—
d-Carvone - - - - - -	—	190	72	174	110	—	162	—	—

p-Chloroacetophenone	—	231	—	—	—	—	—	—	143
p-Chlorobenzophenone	—	—	—	—	106	—	—	—	—
Cinnamal acetophenone	—	218	135	—	157	—	—	—	—
Cinnamyl acetone	—	222	153	—	180	—	186	—	—
Cycloheptanone	108	148	—	—	—	—	—	—	—
Cyclohexanone	118	162	91	146	77	—	166	—	—
Cyclo-octanone	—	163	—	—	—	—	—	—	—
Cyclopentadecanone	—	105	—	—	—	—	—	—	—
Cyclopentanone	190	**146**	56	154	55	—	—	—	—
Desoxybenzoin, *see Phenyl benzyl ketone*									
Diacetone alcohol	—	202	56	—	—	—	—	—	—
Diacetyl	53(m)	315	**238d**	—	239	—	278	—	—
Dibenzyl ketone	162(m)	100	124	—	120	—	—	—	—
Di-*iso*-butyl ketone	—	66	—	—	—	—	122	—	—
Dicinnamal acetone	—	208	—	—	—	—	—	—	—
Diethyl ketone	31(m)	156	—	144	Oil	—	139	72	—
2 : 4-Dihydroxyacetophenone	—	—	—	>*290*	—	—	—	193	—
2 : 6-Dihydroxyacetophenone	—	—	—	—	—	—	—	146	—
2 : 4-Dimethoxyacetophenone	—	—	—	—	—	—	—	118	—
Di-*n*-propyl ketone	—	75	—	—	—	—	133	—	—
Di-*iso*-propyl ketone	—	88	—	—	—	—	—	—	—
Ethyl acetoacetate	—	93	—	—	—	154	133	—	97
Ethyl *n*-butyl ketone	—	—	—	—	—	—	—	—	—

KETONES (cont.)

	Benzaldehyde	2 : 4-Dinitro-phenylhydrazine	Hydroxylamine hydrochloride	*p*-Nitro-phenylhydrazine	Phenyl-hydrazine	4-Phenyl-semicarbazide	Semicarbazide hydrochloride	*p*-Thiocyano-phenylhydrazine hydrochloride	Thio-semicarbazide
Ethyl *iso*-butyl ketone	—	75	—	—	—	—	143	—	—
Ethyl *n*-heptyl ketone	—	—	—	—	—	—	101	—	—
Ethyl levulate	—	101	—	—	103	118	150	—	—
Ethyl oxalacetate	—	—	—	—	—	—	162	—	—
Ethyl oxalmalonate	—	128	—	—	—	—	—	—	—
Ethyl *n*-propyl ketone	—	130	—	—	—	—	110	—	—
Ethyl *iso*-propyl ketone	—	112	—	148	—	—	80	—	—
Fenchone	—	140	167	—	—	—	183	—	—
Fluorenone	—	284	196	269	151	—	—	—	—
Furil	—	—	—	—	184	—	—	—	—
Furoin	—	216	161	—	80	—	—	—	—
Galloacetophenone	—	—	—	—	—	—	—	192	—
α-Hydrindone	113	258	144	235	126	—	233	—	—

o-Hydroxyacetophenone	—	—	70	—	112	—	—	158	—
m-Hydroxyacetophenone	—	—	—	—	—	—	195	151	—
p-Hydroxyacetophenone	—	261	145	—	151	—	199	—	—
p-Iodoacetophenone	—	—	—	—	—	—	—	169	—
α-Ionone	—	150	90	—	—	—	137	—	—
β-Ionone	—	—	—	—	—	—	149	—	—
Levulinic acid	123(m)	206	96	175	108	187	—	156	—
l-Menthone	Oil	146	59	—	53	—	184	—	157
Mesityl oxide	—	203	—	133	—	—	156	—	—
o-Methoxyacetophenone	—	—	—	—	114	—	183	111	—
p-Methoxyacetophenone	—	220	87	195	142	—	197	146	—
o-Methylacetophenone	—	159	61	—	—	—	212	—	—
m-Methylacetophenone	—	—	57	—	—	—	205	—	—
p-Methylacetophenone	—	248	88	*198*	96	—	208	145	—
Methyl *n*-amyl ketone	—	89	—	—	—	—	123	83	—
Methyl *iso*-amyl ketone	—	95	—	—	—	—	—	64	—
Methyl *n*-butyl ketone	—	106	—	88	—	—	122	88	—
Methyl *iso*-butyl ketone	—	95	—	—	—	—	130	89	—
Methyl *tert*-butyl ketone	—	—	77	—	—	—	157	88	—
2-Methyl cyclohexanone	—	136	43	132	—	—	196	—	—
3-Methyl cyclohexanone	122	155	Oil	*119*	94	—	191	—	—
4-Methyl cyclohexanone	99	—	39	128	—	—	197	—	—

KETONES (cont.)

	Benzaldehyde	2 : 4-Dinitro-phenylhydrazine	Hydroxylamine hydrochloride	p-Nitro-phenylhydrazine	Phenyl-hydrazine	4-Phenyl-semicarbazide	Semicarbazide hydrochloride	p-Thiocyano-phenylhydrazine hydrochloride	Thio-semicarbazide
Methyl cyclohexyl ketone	—	140	—	—	—	—	—	—	—
Methyl *n*-decyl ketone	—	—	—	—	—	—	—	—	—
Methyl ethyl ketone	—	111	Oil	128	Oil	—	*146*	105	—
Methyl *n*-heptyl ketone	—	—	—	—	—	—	—	—	—
Methyl *n*-hexyl ketone	—	58	—	93	—	95	122	—	—
Methyl *iso*-hexyl ketone	—	77	—	—	—	—	—	—	—
Methyl *n*-nonyl ketone	—	63	45	91	Oil	—	122	—	—
Methyl *n*-octyl ketone	—	—	—	—	—	—	119	—	—
Methyl *n*-propyl ketone	—	143	—	117	Oil	—	108	94	—
Methyl *iso*-propyl ketone	—	117	—	109	—	—	112	97	—
Methyl *n*-undecyl ketone	—	69	57	102	—	—	123	—	—
m-Nitroacetophenone	—	—	—	—	128	—	—	—	—
p-Nitroacetophenone	—	—	—	—	132	—	—	—	—
Phenyl benzyl ketone	102	204	98	163	116	—	148	—	—

Pinacolone	41	125	79	—	Oil	—	158	—	—
Propiophenone	Oil	191	53	—	—	—	176	—	—
n-Propyl *iso*-butyl ketone	—	—	—	—	—	—	122	—	—
n-Propyl *iso*-propyl ketone	—	—	—	—	—	—	119	—	—
Pulegone	Oil	147	119	—	—	—	—	—	—
Pyruvic acid	—	218	—	220	192	—	222	191	—
α-Tetralone	105	*257*	103	*231*	84	—	226	—	—
α-Thujone	—	—	—	—	—	—	186	—	—
β-Thujone	Oil	—	55	—	—	—	174	—	—
Vanillal acetone	—	230	—	—	128	—	—	—	—

MERCAPTANS

	2 : 4-Dinitro-chlorobenzene	Sulphone
Allyl mercaptan	72	—
n-Amyl mercaptan	80	83
iso-Amyl mercaptan	59	95
Benzyl mercaptan	130	183
p-Bromophenyl mercaptan	142	190
n-Butyl mercaptan	66	92
iso-Butyl mercaptan	76	106
Cetyl mercaptan	91	105
p-Chlorophenyl mercaptan	123	170
o-Cresyl mercaptan	101	155
m-Cresyl mercaptan	91	145
p-Cresyl mercaptan	103	190
Cyclohexyl mercaptan	148	172
Decyl mercaptan	85	93
Dimethylene dimercaptan	248	—
Diphenyl mercaptan	146	170
Ethylene thiohydrin	101	—
Ethyl mercaptan	115	160
Furfuryl mercaptan	130	—
Heptyl mercaptan	82	101
Hexamethylene dimercaptan	218	—
Hexyl mercaptan	74	97
Lauryl mercaptan	89	101

MERCAPTANS (cont.)

	2:4-Dinitro chlorobenzene	Sulphone
α-Methyl dimethylenemercaptan	226	—
Methyl mercaptan	128	190
α-Naphthyl mercaptan	176	—
β-Naphthyl mercaptan	145	—
Nonyl mercaptan	86	92
Octyl mercaptan	78	98
Pentamethylene dimercaptan	170	—
Phenyl ethyl mercaptan	90	134
Phenyl mercaptan *	121	161
n-Propyl mercaptan	81	128
iso-Propyl mercaptan	95	141
Tetramethylene dimercaptan	176	—
Thienyl mercaptan	119	143
Trimethylene dimercaptan	194	—
Undecyl mercaptan	90	97

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* Phenyl mercaptan also yields a derivative with phenyl *iso*-cyanate melting at 129° (*Ind. Eng. Chem.* (*Anal.*), **16**, 304 (1944)).

NITRILES

The nitriles listed in this table are those which have actually been characterised by the use of phenyl *iso*-thiocyanate after reduction to amines (*Ind. Eng. Chem.* (*Anal.*) **13**, 830 (1941)). Other nitriles may be expected to yield the corresponding amines as listed on pp. 127 to 135. α-Naphthyl *iso*-thiocyanate has been included in this table, since, although it has not been applied in precisely this manner, more useful results are to be anticipated (*see p.* 82).

	α-Naphthyl *iso*-thiocyanate	Phenyl *iso*-thiocyanate
Acetonitrile - - - - -	121	106
Benzonitrile - - - - -	172	147
n-Butyronitrile - - - -	109	65
iso-Butyronitrile - - - -	137	82
n-Capronitrile - - - - -	79	77
iso-Capronitrile - - - -	79	112
Glutaronitrile - - - - -	—	148
β-Naphthonitrile - - - -	—	140
Propionitrile - - - - -	103	63
Succinonitrile - - - - -	—	168
o-Tolunitrile - - - - -	—	179
p-Tolunitrile - - - - -	—	144
n-Valeronitrile - - - -	103	69
iso-Valeronitrile - - - -	97	102

PHENOLS

	Acetic anhydride	Benzoyl chloride	Chloroacetic acid	3 : 5-Dinitro-benzoyl chloride	Diphenylcarbamyl chloride	α-Naphthyl *iso*-cyanate	*p*-Nitrobenzoyl chloride	*p*-Nitrobenzyl bromide	Phenyl *iso*-cyanate	Picric acid	*p*-Toluene-sulphonyl chloride	1 : 3 : 5-Trinitrobenzene	*p*-Xenyl *iso*-cyanate
1-Aceto-2-naphthol - - -	—	86	145	—	—	—	—	—	—	—	—	—	—
2-Aceto-1-naphthol - - -	107	128	130	—	—	—	—	—	—	—	—	—	—
p-*n*-Amylphenol - - - -	—	51	90	—	—	—	—	—	—	—	—	—	—
p-*iso*-Amylphenol - - - -	—	—	—	—	—	—	—	—	—	—	—	—	—
p-*tert*-Amylphenol - - - -	Liq.	61	—	—	—	—	—	—	108	—	54	—	—
o-Bromophenol - - - - -	Liq.	—	**142**	—	—	129	—	110	—	—	78	—	—
m-Bromophenol - - - - -	Liq.	86	**108**	—	—	—	—	—	—	—	53	—	—
p-Bromophenol - - - - -	21	102	**157**	—	—	169	—	—	144	—	94	—	—
p-*n*-Butylphenol - - - -	—	27	81	—	—	—	68	—	114	—	—	—	—
p-*iso*-Butylphenol - - - -	—	—	125	—	—	—	—	—	—	—	—	—	—
p-*sec*-Butylphenol - - - -	Liq.	Liq.	—	—	—	—	—	—	—	—	—	—	—
p-*tert*-Butylphenol - - -	Liq.	82	86	—	—	—	—	—	149	—	110	—	—
Carvacrol - - - - -	Liq.	—	**151**	—	—	116	51	—	135	—	—	—	166
Catechol - - - - -	65	84	—	152	—	—	169	—	169	122	—	—	decomp
6-Chloro-*m*-cresol ($CH_3 = 1$) - -	Liq.	86	—	—	—	154	—	—	*139*	—	—	—	—

PHENOLS (cont.)

	Acetic anhydride	Benzoyl chloride	Chloroacetic acid	3 : 5-Dinitro-benzoyl chloride	Diphenylcarbamyl chloride	α-Naphthyl *iso*-cyanate	*p*-Nitrobenzoyl chloride	*p*-Nitrobenzyl bromide	Phenyl *iso*-cyanate	Picric acid	*p*-Toluene-sulphonyl chloride	1 : 3 : 5-Trinitrobenzene	*p*-Xenyl *iso*-cyanate
o-Chlorophenol - - - - -	Liq.	Liq.	**144**	—	—	120	—	100	120	81	**74**	—	—
m-Chlorophenol - - - - -	Liq.	71	**109**	—	—	158	—	—	—	—	—	—	—
p-Chlorophenol - - - - -	Liq.	86	**156**	—	—	166	—	—	149	—	**71**	—	—
o-Cresol - - - - - -	Liq.	Liq.	**152**	138	73	142	94	90	144	90	**55**	—	151
m-Cresol - - - - - -	Liq.	55	**103**	165	101	128	90	51	125	—	**51**	—	164
p-Cresol - - - - - -	Liq.	70	**136**	188	94	146	98	88	115	—	**70**	—	198
pseudo-Cumenol - - - -	34	63	132	—	—	—	—	—	111	—	—	—	196
p-Cyclohexylphenol - - - -	35	118	—	168	—	—	137	—	146	—	—	—	—
2 : 4-Dibromophenol - - -	36	98	153	—	—	—	184	—	—	—	—	—	—
2 : 4-Dichloro-1-naphthol - -	75	—	—	—	—	—	—	—	—	—	—	—	—
2 : 4-Dichlorophenol - - -	Liq.	97	**140**	—	—	—	—	—	—	—	—	—	—
1 : 3-Dihydroxynaphthalene - -	55	—	—	—	—	—	—	—	—	—	—	175	—
1 : 4-Dihydroxynaphthalene - -	128	169	—	—	—	—	—	—	—	—	—	—	—
1 : 5-Dihydroxynaphthalene - -	**160**	**235**	—	—	—	—	—	—	—	—	—	—	—
1 : 8-Dihydroxynaphthalene - -	155	175	—	—	—	—	—	—	—	—	—	—	—
2 : 7-Dihydroxynaphthalene - -	136	139	—	—	**176**	—	—	—	—	—	150	**162**	—

2 : 4-Dinitrophenol	**72**	132	—	—	—	—	—	248	—	—	121	—	—
o-Ethylphenol	—	39	141	108	—	—	57	—	141	—	—	—	—
m-Ethylphenol	Liq.	52	75	—	—	—	68	—	139	—	—	—	—
p-Ethylphenol	Liq.	60	97	132	—	128	81	—	120	—	—	—	—
Eugenol	29	**70**	**100**	131	108	122	81	54	96	63	85	—	—
iso-Eugenol	80	106	—	158	—	150	109	—	—	47	—	70	—
Guaiacol *see* o-*Methoxyphenol*													
p-*n*-Heptylphenol	—	—	94	—	—	—	—	—	—	—	—	—	—
Homocatechol	58	58	—	—	—	—	—	—	166	—	—	—	193
iso-Homocatechol	—	—	—	—	—	—	—	—	174	—	—	—	—
Hydroquinone *see Quinol*													
o-Hydroxybenzaldehyde	39	—	132	—	—	—	124	—	133	—	63	—	—
m-Hydroxybenzaldehyde	76	38	148	—	—	—	—	—	159	—	—	—	—
p-Hydroxybenzaldehyde	—	90	198	—	—	—	—	—	136	—	—	—	—
o-Hydroxybenzoic acid	**135**	—	191	—	—	—	205	—	—	—	—	—	—
m-Hydroxybenzoic acid	**133**	—	206	—	—	—	—	—	—	—	—	—	—
p-Hydroxybenzoic acid	**191**	—	278	—	—	—	—	—	—	—	—	—	—
o-Iodophenol	—	—	135	—	—	—	—	—	—	—	—	—	—
m-Iodophenol	—	—	115	—	—	—	—	—	—	—	—	—	—
p-Iodophenol	32	119	156	—	—	—	—	—	168	—	—	—	—

PHENOLS (cont.)

	Acetic anhydride	Benzoyl chloride	Chloroacetic acid	3 : 5-Dinitro-benzoyl chloride	Diphenylcarbamyl chloride	α-Naphthyl *iso*-cyanate	*p*-Nitrobenzoyl chloride	*p*-Nitrobenzyl bromide	Phenyl *iso*-cyanate	Picric acid	*p*-Toluene-sulphonyl chloride	1 : 3 : 5-Trinitrobenzene	*p*-Xenyl *iso*-cyanate
Mesitol	Liq.	62	132	—	—	—	—	—	142	—	—	—	—
o-Methoxyphenol	Liq.	57	**116**	141	—	118	93	64	136	87	**82**	—	—
m-Methoxyphenol	Liq.	—	116	—	—	129	—	—	—	—	—	—	—
p-Methoxyphenol	32	87	111	—	—	—	—	—	—	44	—	—	—
2-Methyl-4-ethylphenol	—	—	125	—	—	—	—	—	—	—	—	—	—
3-Methyl-4-ethylphenol	—	—	131	—	—	—	—	—	—	—	—	—	—
4-Methyl-2-ethylphenol	—	—	133	—	—	—	—	—	—	—	—	—	—
α-Naphthol	49	56	**192**	217	—	152	**143**	140	178	189	**88**	178	190
β-Naphthol	72	107	**154**	210	**141**	157	169	107	155	156	**125**	158	—
1-Nitro-2-naphthol	61	—	—	—	—	—	—	—	—	—	—	—	—
6-Nitro-1-naphthol	121	148	—	—	—	—	—	—	—	—	—	—	—
o-Nitrophenol	39	59	—	—	114	113	—	130	*126*	—	**83**	—	—
m-Nitrophenol	56	95	—	—	—	167	—	—	129	—	—	—	—
p-Nitrophenol	82	142	—	188	—	151	159	187	148	—	**97**	—	—
Orcinol	25	88	217	190	—	160	214	—	154	92	—	—	196

Phenol - - - - -	Liq.	**69**	**99**	146	105	133	127	91	126	83	**96**	—	173
o-Phenylphenol - - - -	63	76	—	—	—	—	—	—	—	—	65	—	—
m-Phenylphenol - - - -	—	61	—	—	—	—	—	—	—	—	53	—	—
p-Phenylphenol - - - -	88	149	—	—	—	—	—	—	168	—	179	—	—
Phenyl salicylate *see Salol*													
Phloroglucinol - - - -	105	174	—	162	—	—	283	—	191	—	—	—	—
Pyrogallol - - - - -	**165**	90	198	205	212	—	230	—	173	—	—	163	—
Quinol - - - - - -	**123**	**205**	250	317	—	—	258	—	224	—	159	—	decomp
Resorcinol - - - - -	Liq.	117	195	201	**130**	—	182	—	164	—	80	232	decomp
Resorcinol monomethyl ether *see m-Methoxyphenol*													
Salicylaldehyde *see* o-*Hydroxybenzaldehyde*													
Salicylic acid *see* o-*Hydroxybenzoic acid*													
Salol - - - - - -	99	81	—	—	144	—	111	87	—	—	—	85	—
Thymol - - - - -	Liq.	33	148	103	—	160	70	**86**	108	—	71	—	194
2 : 4 : 6-Tribromophenol - -	82	81	—	—	—	153	—	164	—	—	—	—	—
2 : 4 : 5-Trichlorophenol - -	—	93	157	—	—	—	—	—	—	—	—	—	—
2 : 4 : 6-Trichlorophenol - -	Liq.	70	—	—	—	—	106	—	—	—	—	—	—

PHENOLS (cont.)

	Acetic anhydride	Benzoyl chloride	Chloroacetic acid	3 : 5-Dinitro-benzoyl chloride	Dimethylcarbamyl chloride	α-Naphthal *iso*-cyanate	*p*-Nitrobenzoyl chloride	*p*-Nitrobenzyl bromide	Phenyl *iso*-cyanate	Picric acid	*p*-Toluene-sulphonyl chloride	1 : 3 : 5-Trinitrobenzene	*p*-Xenyl *iso*-cyanate
Vanillin	78	78	189	—	—	—	—	124	—	—	—	—	—
1 : 2-Xylen-3-ol	—	—	187	—	—	—	—	—	176	—	—	—	—
1 : 2-Xylen-4-ol	—	59	163	182	—	142	—	—	**120**	84	—	—	183
1 : 3-Xylen-2-ol	—	—	140	159	—	176	—	—	133	53	—	—	198
1 : 3-Xylen-4-ol	—	38	**142**	**165**	—	135	105	—	**102**	—	—	—	184
1 : 3-Xylen-5-ol	—	24	111	195	—	—	—	—	**150**	—	83	—	150
1 : 4-Xylen-2-ol	Liq.	61	118	137	—	173	87	—	162	—	—	—	162

SULPHONAMIDES

	Xanthydrol
p-*n*-Amyl benzene sulphonamide	165
Benzene *m*-disulphonamide	170
Benzene sulphonamide	206
p-*n*-Butyl benzene sulphonamide	186
2 : 4-Dimethyl benzene sulphonamide	188
2 : 5-Dimethyl benzene sulphonamide	176
3 : 4-Dimethyl benzene sulphonamide	190
p-Ethyl benzene sulphonamide	196
o-Methyl benzene sulphonamide	183
p-Methyl benzene sulphonamide	197
p-*n*-Propyl benzene sulphonamide	200
Saccharin	199
Sulphamide ($NH_2SO_2NH_2$)	183
Sulphanilamide	208
2 : 4 : 6-Triethyl benzene sulphonamide	Nil
2 : 4 : 6-Trimethyl benzene sulphonamide	204

SULPHONIC ACIDS

	Benzyl *iso*-thio-urea hydrochloride
m-Aminobenzene sulphonic acid	*148*
p-Aminobenzene sulphonic acid	182
1-Amino-8-naphthol-3 : 6-disulphonic acid	312d.
Anthraquinone-2-sulphonic acid	211
Benzene *o*-disulphonic acid	206
Benzene *m*-disulphonic acid	214
Benzene sulphonic acid	148
Benzthiazol-2-sulphonic acid	171
Benzylaminoazobenzene-*p*-sulphonic acid	*Nil*
α-Bromocamphor-α-sulphonic acid	134
d-Camphor sulphonic acid	210
p-Chlorobenzene sulphonic acid	175
m-Diethylaminobenzene sulphonic acid	182
2 : 4-Dinitro-1-naphthol-7-sulphonic acid	*128*
Diphenyl-*pp′*-disulphonic acid	171
Ethyl sulphonic acid	115
8-Hydroxyquinoline-5-sulphonic acid	*197*
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Naphthalene-1 : 5-disulphonic acid	*257*
Naphthalene-1 : 6-disulphonic acid	81d.
Naphthalene-2 : 6-disulphonic acid	256
Naphthalene-2 : 7-disulphonic acid	205d.
Naphthalene-1-sulphonic acid	137
Naphthalene-2-sulphonic acid	191

SULPHONIC ACIDS (cont.)

	Benzyl *iso*-thio-urea hydrochloride
Naphthalene-1 : 3 : 5-trisulphonic acid	*215d.*
1-Naphthol-3 : 6-disulphonic acid	*217*
1-Naphthol-4 : 8-disulphonic acid	205
2-Naphthol-3 : 6-disulphonic acid	233
2-Naphthol-6 : 8-disulphonic acid	*228*
1-Naphthol-2-sulphonic acid	**170**
1-Naphthol-4-sulphonic acid	103
2-Naphthol-6-sulphonic acid	**217**
2-Naphthol-8-sulphonic acid	*218*
2-Naphthylamine-4 : 8-disulphonic acid	210d.
2-Naphthylamine-6 : 8-disulphonic acid	276d.
1-Naphthylamine-4-sulphonic acid	195d.
1-Naphthylamine-5-sulphonic acid	175d.
1-Naphthylamine-8-sulphonic acid	300d.
2-Naphthylamine-6-sulphonic acid	330d.
m-Nitrobenzene-sulphonic acid	**146**
Phenol-*p*-sulphonic acid	**169**
Phenylhydrazine-*p*-sulphonic acid	*Nil*
N-Phenyl-1-naphthylamine-8-sulphonic acid	182-9d.
Salicylsulphonic acid	**204**
Sulphanilic acid *see* p-*Aminobenzene sulphonic acid*	
o-Sulphobenzoic acid	**206**
m-Sulphobenzoic acid	Oil
p-Sulphobenzoic acid	213
Toluene *o*-sulphonic acid	170
Toluene *p*-sulphonic acid	**182**
p-Toluidine-*m*-sulphonic acid ($CH_3=1$)	*168*
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